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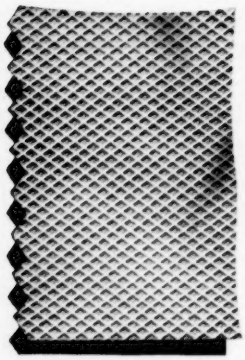

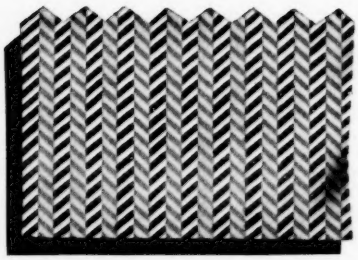

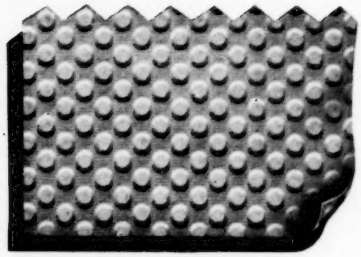

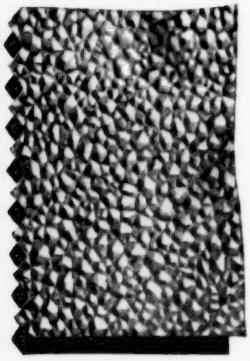

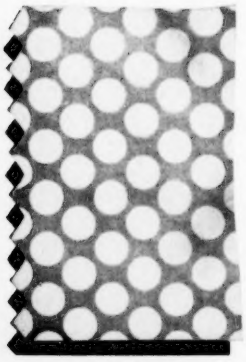

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Fundamental Improvements in Regenerated Cellulose Fiber Structure*

N. Drisch and L. Soep†

Present Man-Made Fibers *vs.* Natural Cellulose Fibers

If we compare the existing man-made cellulose fibers with natural ones, we observe the most marked differences to be the following: (*1*) Man-made cellulose fibers have an elongation at rupture which is generally higher than that of natural fibers. It should be noted that this high elongation was a necessity for its initial use as a silk substitute, because high elongation is a condition *sine qua non* in the case of use for crepe yarns. (*2*) The mean D.P. of the man-made fibers is low, and the cellulose molecule has been considerably degraded. (*3*) The structure of the fibers is totally different. More particularly, the dimensions and the relative importance of the organized regions are less in the case of man-made fibers. (*4*) Man-made cellulose fibers absorb more water than the natural ones. This increased affinity for water causes an important lowering of the breaking strength of fibers in the moist state—*i.e.*, of at least 40%. This is not due to the fact that the nature of the organized regions (crystalline network) is different in the two cases, because mercerization of natural cellulose fibers transforms their network completely without materially affecting their wet strength.

A considerable amount of research work has been done to improve the man-made cellulose fibers—that is, to produce fibers that are more like natural fibers. Remarkable results have been obtained in the fields of high tenacity and low swelling in water, whereas the big stumbling block has been the improvement of the internal structure. Also, a considerable improvement of one quality has often been obtained at the expense of another quality.

The purpose of the present work was to obtain an over-all improvement, and the particular aim was to produce fibers of improved structure.

Previously the present writers stressed that the existing man-made cellulose fibers compared favorably with natural fibers in certain respects, but in other ways they were still distinctly inferior.

By using as the cellulosic raw material pulps having a more regular molecular distribution [3] and obtained by extraction of short chains, man-made fibers having much better properties could be produced.

Rose [8] reviewed the limitations in the production of man-made cellulose fibers of high tenacity: (*1*) by increasing the relative importance of the skin of the filaments in the conventional viscose process, whereby the stretchability is increased and yarns with higher tenacity are produced (usual process for tire yarns); and (*2*) by spinning very fine filaments from normal viscoses in concentrated acid, leading to yarns of very high tenacity but of low elongation and poor loop strength and with low affinity for direct dyes. In view of the above, it is not astonishing that the last-mentioned yarns aroused little practical in-

* Presented at the 1952 Annual Meeting of Textile Research Institute in New York City, Nov. 17, 1952.

† Research Center, Comptoir des Textiles Artificiels, Paris, France.

terest. Recent patents mentioned some improvements of the mechanical properties of man-made fibers owing to a change of the thickness of the skin by a modification of the spinning process. Gains of about 20% of the tenacity may be obtained [2].

However, it appeared very difficult to obtain further improvements from all points of view and to produce man-made cellulose fibers having a combination of good properties and being similar to, if not better than, natural cellulose fibers.

New Fibers

A study was made of the causes of the "failures" of the existing fibers, and also a complete review of the knowledge of their fine structure compared with that of the natural fibers. This research resulted in the development of a new process for the manufacture of fibers having properties that are distinctly different from those of known man-made fibers.

It became evident that the chemistry of viscose making and spinning needed an overhaul. The conventional methods for the preparation of viscose had changed only slightly since the days of Cross and Bevan. On the other hand, Muller's spinning bath, which momentarily had been threatened by the development of Lilienfeld, had maintained its position.

It appeared bold to endeavor to improve the properties of man-made cellulose fibers without modifying the basic process. A research program was therefore established on the basis of theoretical considerations resulting from recent ideas on the molecular structure of native celluloses and on the properties of concentrated solutions of cellulose xanthate [6].

The process that developed from this research, which will be described more completely hereafter, has been covered by a group of patents [4]. Since the authors wanted to test very thoroughly the possibilities revealed by laboratory-scale production, the process remained for a long time in the pilot division. Only recently has industrial production started in the semiworks department.

The major aim in developing these new fibers was to produce man-made fibers showing in combination the following properties: very high tenacity in the dry and wet state, together with satisfactory elongation; high loop strength; low swelling in water; high affinity to direct dyes; and good fatigue-resistance.

Previous analyses showed that the major deficiencies of man-made cellulose fibers were: too low degree of polymerization of the cellulose; greater dispersion of the lengths of the molecular chains; differences in structure between different layers of the individual filaments; and different crystalline structure.

It seemed easy to improve in combination the first three factors, and interesting results had been obtained previously in this sense. Improvement of the microstructure remained the most difficult.

Special Spinning Solutions

It can be shown that if cotton fiber is carefully mercerized, depolymerized, and then treated with CS_2, the cellulose that can be regenerated from the fibrous xanthate thus obtained still has very good tensile properties. Whereas the initial cotton fiber shows a tenacity dry/tenacity wet = 0.9 for D.P. = 3000, the regenerated cellulose, having a D.P. of 500, preserves in the wet state about 90% of the dry strength [7].

Apparently the dissolving of the cellulose xanthate, which is necessary for the spinning operation, disorganizes completely the structure of natural cellulose, which without the dissolution is quite resistant to even a severe attack of the cellulose as far as the ratio of the tenacities is concerned.

The authors therefore considered the means for a limited disintegration of the cellulose material, allowing for the rebuilding of molecular assemblies in fiber form, the formed fibers containing fibrils similar to those in natural cellulose.

The reaction of alkali-cellulose with CS_2 is a rather well-known topochemical reaction, the CS_2 acting primarily on the end-fringes of the structure elements. The fixation of the CS_2 groups causes the formation of hydrophilic groups which attract water molecules, thereby swelling the elements more and more and finally separating the chains forming the structure elements [5].

Many research workers have studied methods which should enable us to determine the structure of cellulose in concentrated solution [1, 9, 10]. Unfortunately, up to the present time it has not been possible to determine this structure definitely, and in this respect we were strictly limited to theoretical considerations. However, admitting these provisionally, we have tried to construct new fibers on this basis.

Our purpose was to provide means to produce a xanthation with a rather high proportion of CS_2, which reacts primarily with the surface layer of the

structure elements and to a lesser extent with the inner part. These elements, having a strongly hydrophilic surface layer, should be dispersible in water or in dilute caustic without complete disconnection of the chains forming the elements.

It may be admitted that the rapid increase of the viscosity of the solution of cellulose of high D.P. is due to the fact that the activity region of the dissolved cellulose increases in proportion to a certain power of the length of the molecules, or, alternatively, is due to the more rapid increase of the number of solvent molecules adsorbed per molecule of cellulose with the greater length of the latter molecule. On this basis, it may then be admitted that the spatial swelling of the crystalline xanthate assemblies during the adsorption of the solvent is the more limited the higher the D.P. of the cellulose, the intermolecular forces of attraction simply being reduced during this process but not completely destroyed. Moreover, it is almost certain that the cellulosic chains, which are completely liberated from each other in dilute solutions, tend to form helices and folds, whereas in jellies of high viscosity as described, the residual interactions between the molecular chains in an initially crystalline assembly allow these chains, according to the limited degree of swelling, to preserve a much more rectilinear form.

It has been found to be feasible to obtain cellulose xanthate dispersions of this kind. These dispersions (jellies) have a marked structural viscosity, but nevertheless they can be filtered and spun. They are more similar to gels than to real colloidal solutions. It is absolutely essential to use cellulose materials of high D.P. which have no short chains, and also to avoid heterogeneous depolymerization of the chains during the different phases of the preparation of viscose. From these xanthate jellies fibers may be obtained which have a submicroscopic structure very similar to that of natural cellulose and markedly different from that of all known man-made cellulose fibers.

These jellies are spun under conditions which cause a homogeneous coagulation, and result in a very fine homogeneous fibril structure.

The dispersions according to the process are prepared from special pulps which have, for instance, the following properties: *alpha*-cellulose content, 98.2%; solubility in 7% caustic soda lye at 90°C, 1.8%; mean D.P., 850; chains with a D.P. of 250–500, 22%; and chains with a D.P. below 250, 2.8%.

The xanthation is effected in the complete absence of oxygen. The dispersions obtained from this xanthate, with a caustic alkali content of 5%–8%, show a viscosity of 250–1,000 poises, and the D.P. of the cellulose in the dispersion is at least 550 [4].

During the regeneration, the rebuilt cellulose assembly will assume a structure reproducing at least in part the initial one, and the orientation of the chains and the formation of new linkages between them will be largely favored by the fact that there is a preservation of the greater part of the rectilinear form of the chains.

Spinning of BX Yarn

According to the particular conditions of coagulation, the properties may be varied extensively—*i.e.*, to increase either the tensile or the elastic properties.

It should be stressed that if these special cellulose xanthate solutions are spun under conditions which are usual for normal viscoses, the filaments obtained will not even be equivalent to normal rayons. It was also necessary to develop improved spinning techniques.

In fact, if these solutions are subjected to the action of a bath dehydrating the formed gel and subsequently regenerating the cellulose, the rebuilt fibrils will possess an excellent structural organization—*i.e.*, the molecules may be lined up almost in parallel; however, the interaction between the fibrils, causing the transverse cohesion of the fiber, is very weak and the properties of it are far inferior to the properties of fibers obtained from the usual solutions, containing cellulose of lower D.P.

It is possible that our theoretical considerations may be criticized, but in any event our work has allowed us to obtain greatly improved filaments, which will be described in detail hereafter.

We have chosen in this research to adopt as a coagulating bath a concentrated solution of H_2SO_4 having a strength which is a function of the degree of xanthogenation of the dissolved cellulose. The sulfuric acid acts as a plasticizer owing to the limited solubility of the xanthate in the acid, and, moreover, the dehydration of the surface portion of the regenerated fibrils allows the hydroxyl groups of nearby fibrils to link up, thereby forming assemblies having a pronounced cohesion.

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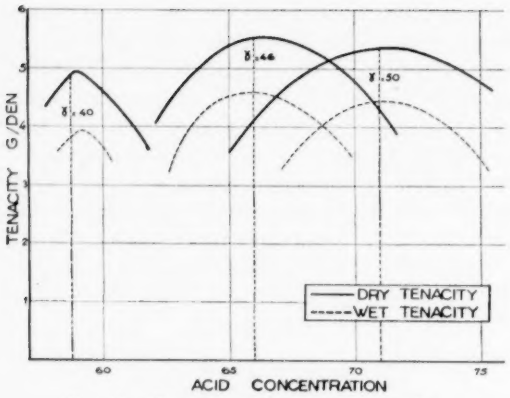

FIG. 1. *Tenacity* vs. *acid concentration.*

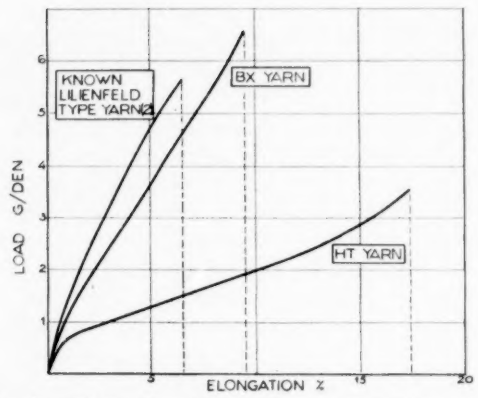

FIG. 2. *Work till rupture value* (= *area under curve*).

fore, it is essential to avoid the presence of short chains, because these tend to dissolve in the spinning bath, thereby affecting unfavorably the possible degree of stretching of the coagulated gel.

The basis of our improved process is to stretch-spin in a strong sulfuric acid bath an adequate, carefully prepared viscose, obtained from a pulp of cellulose of high D.P. and containing only a small percentage of short chains, and to take precautions that practically no depolymerization takes place, neither during the chemical part of the production of filaments nor during the treatment of freshly spun yarn. The γ values of the viscose (number of bound CS_2 groups per 100 C_6) should be related to the sulfuric acid concentration, C, of the bath by the empirical linear formula $C = 1.26\gamma + 8$, with a tolerance of 3%, or preferably 2%.

As a matter of fact, it can be shown that for a given γ the tenacities show a maximum value according to the above-mentioned formula (Figure 1). A discrepancy of $\pm$ 3% affects the tenacity by 0.5–1 g./den., the curve becoming more flat-topped for higher γ; a discrepancy of $\pm$ 2% affects the tenacity only about half of this value. The optimum acid concentration of the bath seems to be about 66%, corresponding to a γ of 46. Figure 2 compares the work till rupture values of this yarn and others, as defined hereafter.

The foregoing considerations apply to spinning at room temperature. Similar results can be obtained at higher γ temperatures, the optimum γ_T (T being the temperature of the bath) being related to γ_{20} by the exponential formula [6]:

$$\gamma_T = \gamma_{20} + (T-20)^{0.7}.$$

Both of the above formulas are empirical, but give practical results, which is in any event the most important thing.

The filaments are stretched at a short distance from the spinneret by a device applying the tension in several steps. One such device has been described in a patent [4], but other devices have also been developed.

The optimum properties are obtained with very fine filaments—for instance, 0.5 den. or less.

The action of the strong sulfuric acid bath on the viscose is materially different from the action of the so-called "Muller bath." When filaments of fine denier are spun in a strong sulfuric acid bath, the penetration of the acid into the liquid viscose veins appears to be rapid enough to form almost immediately a semisolid mass that is completely impregnated with acid and to produce plastic cellulose filaments which can be highly stretched.

Whereas filaments made by the initial Lilienfeld process show internal cracks, apparently due to overstretching in a nonplastic state, our filaments show numerous microcavities (interfibrillar spaces), and these are even useful as far as after treatments are concerned. They explain the relative ease of dyeing.

Another important feature is the long air path of the filaments between the last positive guide-roller and the winding station. During this air path, which may be 5 m. or more in length, the filament bundle remains under tension, without further stretch, and is then relaxed completely. The purpose is to allow a homogenization of the filaments by relaxation of the interior tensions.

The stretched acid-impregnated filaments must be

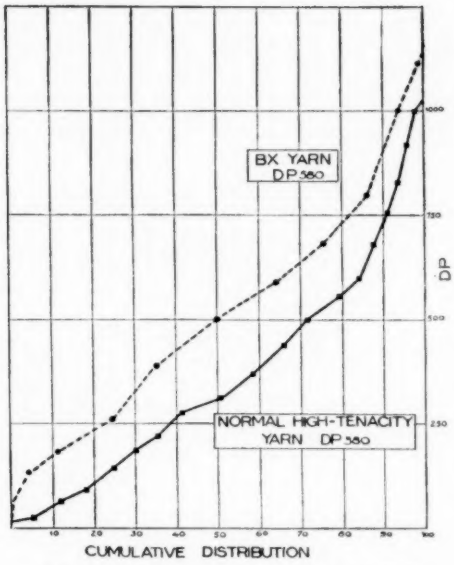

FIG. 3. *Cumulative distribution of D.P.*

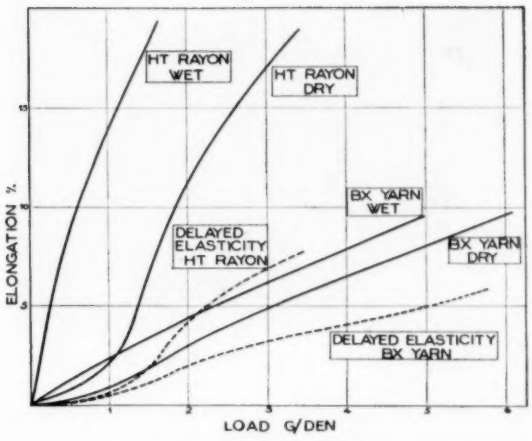

FIG. 4. *Delayed elasticity.*

washed after relaxation, and this operation requires special care. The washing should not be too slow, to avoid degradation of the cellulose by the acid, nor too fast, whereby the sudden deswelling could tend to "explode" the filaments. The conditions of washing have been studied carefully, and apparently the most favorable method is to effect a preliminary washing during a sufficiently long stretch whereby the acid concentration of the jelly decreases to reach a concentration weaker than a few percent. Thereafter the filaments can be wound and finished in cake form as usual, or otherwise.

Properties of BX Yarn

Considering now the properties of the improved filaments, a diagrammatic representation of the distribution of chain lengths in our special filaments (D.P. 580) compared with normal high-tenacity tire yarn (D.P. 320–380) is shown in Figure 3. The entire curve for the special yarn lies on a higher level, but more important is the smaller proportion of chains of low D.P.

Tensile strength *vs.* elongation and elastic properties for our special yarn compared with those for normal HT yarn are shown in Figure 4. The curves for the special yarn are of a different nature, and the delayed elasticity as compared with the elongation to rupture is particularly remarkable.

Table I compares the tensile properties and the swelling of cotton fiber, HT rayon, and our special yarn, BX. The high loop tenacity and the relatively low swelling, especially of the diameter, should be noted, and particularly the very low solubility in 10% caustic, which is of the same magnitude as that of cotton. Even at low temperatures, where the swelling power of caustic is high, the swelling remains moderate. Even caustic of mercerizing strength is not very active. X-ray studies have shown that the orientation is similar to that of highly stretched

TABLE I. CHARACTERISTICS OF COTTON, RAYON HT, AND BX

	Tenacity (g./den.)		Elongation (%)					Solubility (10% NaOH at 20°C)		
	Air-dry	Wet	Air-dry	Wet	Loop tenacity	Filament (den.)	D.P.	(%)	Swelling: weight (%)	Swelling: diameter (%)
Cotton fiber	3.8	4.0	8.0	7.5		1.30	3000	2.5	48	35
Rayon HT	3.4	2.0	21	28	2.6	2.2	380	40	95	72
							400			
Yarn BX	5.8	4.6	10	11	4.0	0.3	580	2	75	46
						0.5	700			

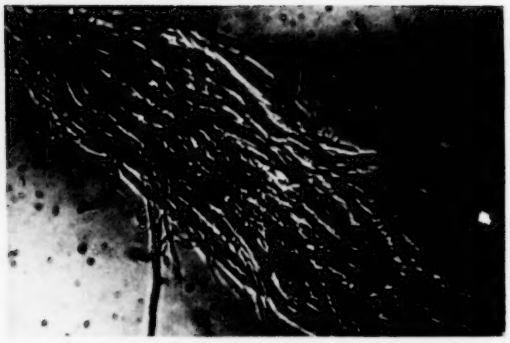

FIG. 5. *Sample of crushed swollen BX fibers.*

rayons, as well as the importance of crystalline regions, but is not much higher. The filaments of the special yarn comprise very fine, more or less felted fibrils, whereas in normal HT yarn the fibrils are coarse and parallel (Figure 5).

A curious phenomenon is that the swelling index in water, which tends rapidly to a minimum with increasing centrifugal force of the bowl, continues to decrease for higher speeds of the bowl and reaches a much lower level than for HT rayon. This phenomenon may be related to the presence of micropores and to the particularly high affinity to direct dyes resulting from these micropores. Cross sections are round instead of serrated as in normal HT rayon. The swelling of the diameter is small.

Particular attention should be given to the property that represents the work to be done till the yarn breaks and is represented by the area under the tenacity-elongation curve. In the old days of Lilienfeld, yarns having a tenacity of 5–5.5 g./den. had been obtained, but they had very low elongation at rupture; of course, the work till rupture value was low. The highest value observed was of the order of 12–15 g./den. (cm./m.). Our yarn has a work till rupture value of the order of 25, which is comparable to that of the best tire yarns (Figure 2).

For years there has been a big controversy about the fatigue-resistance of yarns. Many procedures have been proposed, but the results have frequently been questioned. First of all, the results obtained with different apparatus were not always consistent, not even in rank, and the dispersion of the results was also rather large. Cords of our yarn have been submitted to different fatigue tests—*i.e.*, tests taking into account the flexibility gave highly favorable results owing to the extreme fineness of the individual filaments; and tests embodying cyclic stressing gave results which were of the same order of magnitude as results for usual tire yarns.

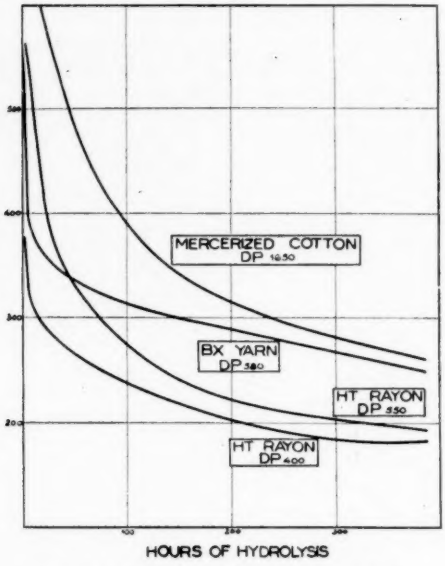

FIG. 6. *Hydrolysis by 2N HCl at 15°C.*

It is important to note that tires have been made which on road tests gave most interesting and promising results.

Our yarn has been submitted to a great number of chemical-resistance tests, since one of our aims was the production of a man-made yarn that could be satisfactorily "tortured" by washing and bleaching procedures.

The authors made tests to compare the BX yarn with high-grade cotton (Egyptian) and with HT rayon. Figure 6 shows the effect of *2N* HCl at 15°C on the D.P. Whereas the D.P. of HT rayon falls to a level of about 200, that of the special yarn falls at first rather rapidly but then the curve changes its shape and follows the curve of mercerized cotton. This indicates that at first the behavior of BX is different from that of cotton because of the initial higher mean D.P. of cotton, but then the behavior becomes similar.

Excellent results have been obtained by repeated washing tests on comparable samples of fabric under the following conditions: Mechanical treatment with a solution containing 10 g./l. of sodium carbonate and

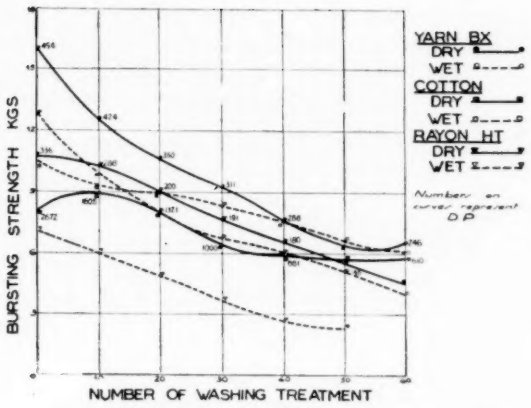

FIG. 7. *Bursting strength vs. number of washings for similar fabrics.*

2 g./l. of Marseille soap, boiling for 1 hr., and then rinsing and bleaching with a sodium hypochlorite solution of 3° active chlorine at 20°C for 15 min.

Figure 7 shows the progressive degradation of the different fabrics after repeated treatment, as measured by the fall of the bursting strength. The curves are parallel, and that for our special yarn constantly remains at a higher level than those for cotton (raw) and HT rayon. The curve for scoured cotton would have been much lower. The wet resistance remains at a very high level even after 50 washings.

Dyeing and Anticrease Treatments

The dyeing behavior is very interesting. Whereas Lilienfeld-type yarns normally resist dyeing, or can only be dyed with heavy expense of dyes, and whereas dark shades can only be obtained exceptionally, our yarn behaves in a completely different way. According to time-adsorption tests made with different dyes, and particularly Sky Blue 6B, the adsorption is more rapid than for HT rayon, although slightly slower than for cotton. However, the final dye adsorption is similar for the different fibers, although the two man-made fibers dye somewhat darker. Dark shades may be obtained.

This proves again that the structure of our yarn is distinctly different from the structure of yarns obtained by the older strong-acid processes.

Beautiful prints may be obtained without any change in the usual procedure.

We have particularly studied the crease-resistance of fabrics of our yarn. Although the yarn is composed of extremely fine filaments (lower than 0.5 den., but even obtention of filaments of 0.1 den. offers no special difficulties), the crease-resistance, which is reputed to decrease with lower denier of individual filaments, is unexpectedly good, even without any special treatment. It may be that the rather high elasticity modulus and the particular microstructure contribute to this result.

However, it may be useful to increase the wrinkle-resistance. In applying known resin sizes, we have discovered that fabrics of our yarn can very easily be made highly wrinkle-resistant. The resin or its constituents can penetrate easily into the filaments and can react there throughout.

Whereas known cellulosic fabrics of fibers having a low elongation, as, for example, cotton, are always more or less degraded by anticrease treatments, as shown by the lowered tenacity and elongation and an increase of the brittleness, the fabrics made of our yarn were not materially weakened by these treatments (Table II).

Uses of BX Yarn

The possible uses of this new fiber will now be considered. In view of the fact that it behaves much more like natural cellulose fibers than known man-made fibers, and seems to be even superior to natural

TABLE II. EFFECT OF ANTICREASE TREATMENTS

	Dry				Wet					
	Tenacity (g./den.)		Elongation (%)		Tenacity (g./den.)		Elongation (%)		Recovery angle (degrees)	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Cotton yarn*	1.55	1.05	8	5	2.0	1.35	10	7	102	145
Fiber BX yarn	4.73	4.86	8	6.5	3.47	3.33	9	7.5	80	157
Standard rayon	1.9	2.2	15	8	0.9	1.2	14	11	84	134

* The yarns were drawn from fabrics which had been submitted to an anticrease treatment.

TABLE III. DIRECT SPINNING

	Tenacity (g./den.) Dry	Wet	Elongation at break (%)	Irregularity (%)
Cotton No. 120	1.72	1.96	7.2	13
Fiber BX yarn No. 120	4.6	3.5	6.2	4.5
Fiber BX yarn No. 200	4.3	3.2	5.8	6.5

fibers from some points of view, we may expect that it will have great possibilities, either alone or in mixtures.

The following possibilities for the use of this fiber will be considered: industrial applications (tires and belts, more particularly) and textile applications.

In tires (and similar uses, of course) good and encouraging results have already been obtained. Cords of unusually high quality can also be obtained.

Although fatigue testing did not show a distinct superiority of the new fibers over standard HT rayon cords, truck tires have been made with quite a saving of yarn and containing up to 20%–25% less rubber (according to increase of tenacity of yarn); they behaved very well in preliminary road tests. Large-scale tests are under way. The authors believe that this yarn will be especially valuable for heavy-duty tires for trucks and planes (see U. S. Patent 2,586,795 [4]).

Recently, certain metallic filaments have been used in the production of heavy-duty tires. It might be suggested that the new fibers would behave similarly to metallic filaments because of their very high resistance and their elastic behavior. Metallic filaments are assembled with a moderate twist, and their resistance under tension is high—*i.e.*, 3.5 g./den.—taking into account the much higher density, whereas the elongation is very low (about 2.5%). The new yarn might be used under similar conditions with low cord twists in order to get the optimum benefit of the high tenacity, while allowing at the same time for elastic deformations to be able to withstand and to absorb sudden shocks.

Since the Lilienfeld-type yarn could never be used until now in tires, our yarn thus represents a very important improvement.

The authors have done a large amount of development work in the textile field and have concentrated on lightweight fabrics made from low-denier yarns. Spinning continuous-filament yarns of low denier offers some practical difficulties which might be surmounted. On the other hand, it is possible to spin heavy bundles of filaments and to staple them in view of conventional spinning, but the extreme fineness of the fibers causes serious problems in carding, combing, etc. Development work on tow-to-top is under way. However, the authors have used direct spinning processes, and have obtained remarkable results.

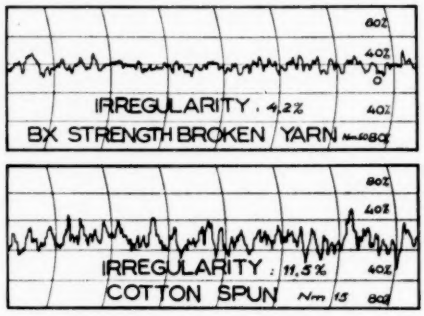

FIG. 8. *Uster-Zellweger diagrams of yarns.*

Stretch-Spinning

Spun yarns of very good quality of, for instance, 40 den. or even 25 den. (no. 240 French = 71 English, or no. 360 French = 106 English) can be obtained without major difficulties.

In Table III cotton is compared with a yarn obtained by stretch-breaking a 1,200-den. bundle of 300 filaments and spinning.

The authors used apparatus developed by a related French firm, the K-11-C machine, where the breaking point of the filaments is localized between the pairs of stretch rollers by a rotating prismatic bar having noncutting edges. The yarns obtained show a remarkable regularity of denier which is very much superior to that of yarns produced by conventional methods from fibers in bulk, and the K-11-C machine allows more particularly for the production of very fine yarns (Figure 8).

Yarns produced in this way may be used to build very lightweight fabrics which are practically impossible to produce with any known cellulose yarn. Fabrics weighing 1½ oz./sq. yd. for women's underwear and fabrics weighing about 2½ oz./sq. yd. for printed goods (dresses) have been made without major difficulties. These fabrics have a permeability equal to that of cotton, and show good washability.

A wide variety of fabrics of this kind have been made. They are resilient and more or less crease-

resistant. These properties can, however, still be strongly enhanced by conventional urea-formaldehyde treatments, whereby the resin penetrates the filaments. Such treatments result in good crease-resistance by repeated washings under commercial conditions, which is required for underwear and ladies' summer dresses.

The treatment with resin gives a "hand" that is very special and seems due to the very fine individual filaments. These are also responsible for the very luxurious appearance of the yarns and fabrics, distinct from and far superior to any known textile product.

Dyeing and printing offer no difficulties. Brilliant shades can be obtained almost as easily as on normal viscose rayons.

The writers have shown that by using particular cellulose xanthate dispersions, obtained from very uniform pulps with a high D.P., it is possible to produce filaments of a remarkable resistance in the dry, but especially in the wet state, showing also satisfactory elongation and fatigue-resistance. These filaments have a particular fibrillar structure.

These filaments have elastic properties and a work till rupture value which are highly satisfactory. They are thus distinct from known high-tenacity man-made cellulose filaments. These properties allow the use of these filaments in all industrial fields where a high resistance combined with a satisfactory fatigue-resistance are required. On the other hand, in the textile field the very small denier of the individual filaments makes possible the production of remarkable fine and regular yarns, with a very acceptable resistance that can support the usual treatments without damage.

The potential improvement of the filaments and the process of making them appears to be enormous, and already our procedure has made substantial progress.*

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* The continued research work conducted after filing the patent applications has resulted in substantial improvement of the process. The tenacities have been improved considerably, and at present we are able to produce industrially yarns having a tenacity of 7 g./den. in the dry state and 5.3 g./den. wet, the elongation at break remaining of the order of 10%. The rapid development of the research work during recent months has prevented us from including these results in this paper.

Aminization of Cotton

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A FEW YEARS AGO it was found that amino groups could be attached to the cellulose of cotton by reacting it with 2-aminoethylsulfuric acid in the presence of sodium hydroxide [2]. A degree of aminization represented by 0.3% to 0.4% nitrogen may be readily obtained by this method. Although this level of aminization is adequate for demonstrating the unique dyeing characteristics and for some experimental work, a number of potential applications of aminized cotton require a higher degree of aminization.

The present paper reports work that has been done to find ways for applying the aminization process to cotton in various forms, such as raw stock, sliver, yarn, and fabric, and to increase the degree of aminization that can be obtained by a single processing. Experiments with compounds related to 2-aminoethylsulfuric acid and with other methods for aminizing cotton are also reported.

Aminization of Cotton in Various Forms

Raw Stock

Aminization of raw stock on a large scale would present many difficulties, but it can be done on a laboratory scale, as illustrated by the following experiment.

Deltapine cotton, 2.5 lbs. taken from the bale, was wetted with a solution composed of 3 kg. of sodium hydroxide, 1.2 kg. of 2-aminoethylsulfuric acid, 15 ml. of wetting agent of the cresylic acid type, and 7.8 kg. of water. After removing the excess solution by centrifuging, the moist cotton was dried and cured for 2 hrs. at 110°C in a forced draft oven, thoroughly washed with tap water, and dried. The aminized cotton was put through an opener and processed into roving of poor quality due to the presence of many neps. The nitrogen content of the fiber was 0.45% on the air-dry basis.

Card Sliver

Cotton sliver can be aminized more conveniently than raw stock, and it might be possible to aminize sliver on a large scale by batchwise or continuous processes. If cotton sliver is immersed in a large excess of the solution used for aminization, it breaks when lifted from the solution. However, when sliver is wetted with just the right amount of solution, it may be lifted about 15 in. from the solution and passed through squeeze rolls to form a ribbon having considerable strength. The amount of solution to use is about 10 times the weight of the sliver. The sliver may then be cured, washed, dried, and converted into yarn.

Card sliver was aminized by the batchwise procedure as follows: A roll of 8 lbs. of S × P cotton card sliver was placed in stainless-steel cans and wetted with a total of 80 lbs. of a solution composed of 25 parts of 2-aminoethylsurfuric acid and 0.4 part of a suitable wetting agent. After the sliver was completely and uniformly wetted with the solution, it was put through rubber squeeze rolls. The pickup of solution was 230%. The sliver was cured in an oven at 110°C for 1 hr., and then washed by soaking in running tap water and passing through squeeze rolls. The sliver may also be washed on a padder by passing it through water several times. The sliver was then air-dried, but it may also be dried in an oven or by passing over steam-heated cans. A control sample was prepared in the same way, except that a solution composed of 25 parts sodium hydroxide, 74.6 parts water, and 0.4 part of the wetting agent was used to wet the sliver. The aminized and control slivers were opened by putting through a drawing frame, returned to the opener, carded, and processed into 15.50 yarn of 2.72 T.M. Yarn was also made from the untreated cotton. The grades of the yarn from the aminized cotton, sodium hydroxide-treated control cotton, and untreated cotton were B +, B +, and A, respectively. The breaking strengths were 384, 409, and 775 g., respectively, and Pressley strength indexes were 5.1, 6.1, and 8.3 lbs./mg., respectively. The aminized cotton contained 0.45% nitrogen on the air-dry basis.

Card sliver of the Bobshaw variety was processed in a similar manner and converted into yarn. The yarn grades for the aminized cotton, sodium hydroxide-treated control cotton, and untreated cotton

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were B, B +, and A −, respectively. Breaking strengths were 249, 263, and 444 g., respectively, and the Pressley strength indexes were 6.0, 6.4, and 7.9 lbs./mg., respectively. The aminized cotton contained 0.45% nitrogen on the air-dry basis. When the aminized sliver was processed into yarn without returning to the opener and recarding, a poor grade of yarn was obtained.

A higher degree of aminization, about 1.0% nitrogen, was obtained by increasing the 2-aminoethylsulfuric acid content of the aminization solution to 20%, but the resulting product was so stiff and felted that no attempt was made to convert it into yarn.

Card sliver was aminized by the continuous process on a small padding machine as follows: The sliver was started through the empty padder at 5 to 15 yds./min., and the solution was then poured into the trough while the sliver was in motion. By this process the sliver became uniformly wetted by the time it reached the squeeze rolls, and did not break as long as the padder was kept going at the proper speed. Curing and other processing were the same as used in the batchwise process described above.

Roving may be processed by the same methods that are used for sliver.

Yarn and Thread

Yarn or thread may be readily aminized in the form of skeins by batch processing, but the practical handling of large quantities might prove difficult. The aminization of yarn and thread is illustrated by the following experiments.

Skeins of 55/3 Sak sewing thread were wetted with a solution composed of 1260 ml. of water, 500 g. of sodium hydroxide, 200 g. of 2-aminoethylsulfuric acid, and 40 g. of wetting agent of the cresylic acid type. The excess solution was removed by centrifugation. The pickup of solution was 170%. The skeins were hung loosely in an oven at 100°C and cured for 1 hr. Each 10-g. skein was then put under a tension of 2.35 kg., washed thoroughly with water while under tension, soured in 1% acetic acid, and again washed with water and air-dried. The resulting yarn had a nitrogen content of 0.42% on the oven-dry basis and dyed uniformly with Kiton Fast Red, an acid wool dye. The breaking strength was 1.9 lbs. The original untreated thread had a breaking strength of 2.0 lbs.

Deltapine cotton in the form of 16s/2 yarn was aminized in the same way as described above. This aminized yarn had a nitrogen content of 0.33% on an air-dry basis. It had a breaking strength of 1354 g. and a Pressley index of 6.60 lbs./mg. The raw, untreated yarn had a breaking strength of 1124 g. and a Pressley index of 7.48 lbs./mg.

In experiments with tire cord, which was aminized under conditions that prevented shrinking, a rather low degree of aminization, about 0.1% nitrogen, was obtained. This was probably due to the tight twist and close construction of the tire cord.

Fabric

Cotton is most conveniently aminized in the form of fabric, and the process may be applied on a pilot-plant scale, as illustrated by the following experiments.

A combined roll of fabric composed of mercerized Osnaburg, 100 × 60 bleached broadcloth, and 48 × 48 bleached sheeting, total weight 29.5 lbs., was padded with a solution composed of 78 lbs. of water, 30 lbs. of sodium hydroxide, and 12 lbs. of 2-aminoethylsulfuric acid. The combined pickup was 97%. The fabric was then cured by passing slowly over rotating steam-heated cans at 10 lbs. excess steam pressure. The surface temperature of the dry cans was about 93°C. The speed was such that the fabric was cured on the cans for a total of about 30 min. The fabrics were then washed on a jig with hot water, soured lightly with very dilute sulfuric acid, neutralized with ammonia, washed again with water, and dried on the cans. The Osnaburg had a nitrogen content of 0.28% on the dry basis, the broadcloth 0.37%, and the sheeting 0.43%. The Osnaburg and sheeting showed gains in warp breaking strength of 8% and 3%, respectively, while the broadcloth showed a loss of 8%.

Another combined roll of fabric, total weight 35 lbs., composed of kier-boiled bleached 80 × 80 print cloth and gray print cloth was padded with a solution composed of 60 lbs. of water, 25 lbs. of sodium hydroxide, 10 lbs. of 2-aminoethylsulfuric acid, and 2 lbs. of a wetting agent of the cresylic acid type. The pickup was 94%. The fabric was then cured by passing it slowly over dry cans at such a rate that the curing time was about 30 min. Small samples of the fabric were taken after it had been on the cans for only 15 min. The steam pressure was 15 lbs. in excess of atmospheric pressure, and the surface temperature of the cans was about 99°C. Washing and

drying was done as described above. The aminized kier-boiled bleached, kier-boiled unbleached, and gray cloth had nitrogen contents of 0.34%, 0.32%, and 0.24%, respectively, on the dry basis. The nitrogen contents of the samples cured for only 15 min. were essentially the same as those obtained for the samples cured 30 min. Warp breaking strengths (strip method; counted yarn) were 46.8, 47.8, and 43.4 lbs., respectively. The untreated gray fabric had a breaking strength of 50.6 lbs.

In order to provide for proper experimental material for future work, a control run was also made which differed only in the omission of the 2-aminoethylsulfuric acid from the solution used to pad the 35 lbs. of fabric, the solution used being composed of 76 lbs. of water, 22 lbs. of sodium hydroxide, and 2 lbs. of wetting agent.

In connection with the experiment described in the last two paragraphs, some of the kier-boiled unbleached print cloth was padded with the aminization solution and then passed rapidly over the steam cans in order to dry it and to cure it to the point where the aminization reaction had just started. The fabric was on the cans about 3 min., and a sample taken at this time had a nitrogen content of 0.04% on the dry basis. At this point the warm fabric was rolled up, wrapped in a sheet of aluminum, and placed in an oven at 100°C for 4 hrs. It was then washed and dried. The nitrogen content was 0.33% on the dry basis. This experiment indicates that drying and curing could be started on steam-heated cans and then completed in an oven or hot box.

Some of the kier-boiled unbleached print cloth that had been aminized was subsequently given a peroxide bleach. The nitrogen content prior to bleaching was 0.32% on the dry basis, and after bleaching it was 0.28%. Similarly, the gray print cloth that had been aminized (nitrogen was 0.24%) was given a 2% caustic boil for 3 hrs. and then a peroxide bleach. The nitrogen content was now 0.19%. This shows that fabric could be aminized prior to kier-boiling or peroxide bleaching without serious loss of amino groups.

Although cotton aminized to the point where it contains 0.3% to 0.4% nitrogen is suitable for demonstrating dyeing properties and for some other experimental demonstrations, certain possible uses, such as anion-exchange material [3, 4], require a higher degree of aminization. In order to make such a fabric available for experimental use, cotton fabric was put through the aminization process three times. Kier-boiled 48 × 44 sheeting, 130 yds. and weighing 38.5 lbs., was padded with a solution composed of 130 lbs. of water, 50 lbs. of sodium hydroxide, and 20 lbs. of 2-aminoethylsulfuric acid. The pickup was 130%. Curing was on steam cans with 32 lbs. steam pressure to give a surface temperature of about 120°C. The time in contact with the cans was about 9 min. After curing, the fabric was washed, dried, and put through the process two more times. A sample after the first aminization contained 0.42% nitrogen on the dry basis, and a sample after the second aminization contained 0.75% nitrogen. The final fabric, after three aminizations, contained 0.92% nitrogen on the dry basis. The warp breaking strength (strip method; counted yarns) was 53.8 lbs., while the breaking strength of the untreated fabric averaged 53.8 lbs. Some subsequent experiments showed that when fabric was put through the aminization step two or more times, the washing between aminization could be omitted, the cured fabric being padded with the aminizing solution directly after curing. It also should be noted here that a study of the effect of processing variables (reported below) has shown that the level of nitrogen obtained in the triply aminized fabric described above can be obtained in one aminization if the sodium hydroxide concentration is increased to 30% and the 2-aminoethylsulfuric acid concentration to 20%.

Effect of Reagent Concentrations and Processing Conditions upon the Degree of Aminization

In the experiments reported in the first part of this paper the aminization solution used was usually 10% 2-aminoethylsulfuric acid in 25% sodium hydroxide. Curing temperatures were in the range of 100°C for times sufficient to complete the aminization reaction. Fabric processed one time under these conditions contained 0.3% to 0.4% nitrogen, a degree of aminization adequate for many experimental uses. However, some potential uses of aminized cotton, such as use as an anion-exchange material [3, 4] or use for conversion to a flame-resistant fabric by reaction with phosphorus compounds, require a higher degree of aminization. Therefore, with the objective of finding a way of obtaining a higher degree of aminization in a single processing and also of increasing the efficiency of the aminization reaction based on the pickup of 2-aminoethylsulfuric acid, an experiment was made including all possible combinations of the following conditions: (*a*) rapid padding with 2 sec. contact with the aminization solution *vs.* soaking for 5 min.

TABLE I. Effects of Concentration of Reagents upon the Degree of Aminization

Concentration of reagents	Time fabric in solution	Squeeze-roll setting	Pickup %	Nitrogen (dry basis) %	Efficiency %
	2 sec.	1.5	159	0.48	28
	2 sec.	2.0	145	0.34	22
	2 sec.	4.0	121	0.34	26
10% 2-AES*	2 sec.	5.0	115	0.34	28
25% NaOH	5 min.	1.5	200	0.52	24
	5 min.	2.0	189	0.48	24
	5 min.	4.0	174	0.41	22
	5 min.	5.0	167	0.41	23
	2 sec.	1.5	163	0.57	33
	2 sec.	2.0	152	0.55	34
	2 sec.	4.0	133	0.51	36
10% 2-AES	2 sec.	5.0	130	0.49	35
30% NaOH	5 min.	1.5	245	0.64	25
	5 min.	2.0	226	0.51	21
	5 min.	4.0	207	0.58	26
	5 min.	5.0	202	0.55	26
	2 sec.	1.5	159	0.59	35
	2 sec.	2.0	151	0.46	29
	2 sec.	4.0	136	0.49	34
10% 2-AES	2 sec.	5.0	133	0.49	35
35% NaOH	5 min.	1.5	254	0.63	23
	5 min.	2.0	245	0.67	26
	5 min.	4.0	222	0.61	26
	5 min.	5.0	212	0.59	26
	2 sec.	1.5	163	0.94	27
	2 sec.	2.0	150	0.82	26
	2 sec.	4.0	131	0.72	26
20% 2-AES	2 sec.	5.0	126	0.61	23
25% NaOH	5 min.	1.5	219	1.14	24
	5 min.	2.0	214	1.11	24
	5 min.	4.0	194	1.01	24
	5 min.	5.0	187	0.93	24
	2 sec.	1.5	170	1.05	29
	2 sec.	2.0	158	0.97	29
	2 sec.	4.0	141	0.94	31
20% 2-AES	2 sec.	5.0	134	0.94	33
30% NaOH	5 min.	1.5	257	0.91	17
	5 min.	2.0	250	0.93	18
	5 min.	4.0	229	0.91	19
	5 min.	5.0	222	0.92	20
	2 sec.	1.5	169	1.04	29
	2 sec.	2.0	157	0.98	29
	2 sec.	4.0	140	0.88	30
20% 2-AES	2 sec.	5.0	137	0.88	30
35% NaOH	5 min.	1.5	267	0.91	16
	5 min.	2.0	246	0.89	17
	5 min.	4.0	223	0.91	19
	5 min.	5.0	218	0.93	20

* 2-AES = 2-aminoethylsulfuric acid.

in the aminization solution prior to putting through the squeeze rolls; (*b*) 10 % *vs.* 20% 2-aminoethylsulfuric acid; (*c*) 25%, 30%, and 35% sodium hydroxide solution; (*d*) squeeze-roll settings of 1.5, 2.0, 4.0, and 5.0 to give various pickups.

TABLE II. Aminization of 80 × 80 Print Cloth

Concentration of reagents	Squeeze-roll setting	Pickup %	Nitrogen (dry basis) %	Efficiency %
20% 2-AES*	3	145.0	0.69	22
25% NaOH	5	134.5	0.66	23
20% 2-AES	3	153.5	0.73	22
30% NaOH	5	143.7	0.69	23
25% 2-AES	3	157.7	0.56	17
30% NaOH	5	167.5†	0.52	15
20% 2-AES	3	160.0	0.57	17
35% NaOH	5	153.0	0.56	17

* 2-AES = 2-aminoethylsulfuric acid.

† Higher pickup of this sample due to improper immersion, necessitating a second pass through the padder.

The fabric used in these experiments was a loosely woven bleached towelling. Curing was done in a forced draft oven for 50 min. at 110°C.

The results are given in Table I. It will be noted that all the factors included in the experiment had some effect on the degree of aminization. It is of special interest to note that allowing the fabric to stand in the solution for 5 min. greatly increased the pickup without proportionately increasing the degree of aminization. In fact, in some cases a decrease in the degree of aminization was observed due to standing for 5 min. in the solution. Due to the fact that standing in the solution increased the pickup without proportionately increasing the degree of aminization, standing had the effect of reducing the chemical efficiency of the process when calculated on the amount of 2-aminoethylsulfuric acid taken up by the fabric. The degree of aminization was almost doubled by the use of 20% 2-aminoethylsulfuric acid instead of 10%. Increasing the sodium hydroxide concentration from 25% to 30% or 35% under most of the conditions resulted in a higher degree of aminization.

The results obtained in the experiments summarized in Table I were used in planning the aminization of 100 yds. of 80 × 80 print cloth. Preliminary to aminizing this amount of print cloth, some experiments were run with small pieces on the same padder. The results are given in Table II. The use of 20% 2-aminoethylsulfuric acid in 30% sodium hydroxide was chosen for the large run described below.

One-hundred yards of 80 × 80 square print cloth that had been previously kier-boiled and bleached was padded with a solution containing 20% 2-aminoethylsulfuric acid, 30% sodium hydroxide, and 0.5%

of a wetting agent of the cresylic acid type. A commercial-sized padder was used at the rate of 50 yds./min., giving a time of contact with the solution of about 1 sec. The pickup was 140%. The fabric was cured on steam cans with a surface temperature of about 120°C. Each part of the fabric was on the cans for about 15 min. The fabric was then washed on a jig with cold water followed by hot water. It was soured lightly with very dilute acetic acid, rinsed with very dilute ammonium hydroxide, and dried. The nitrogen content was 0.68% on the dry basis, a value in good agreement with that obtained with the same fabric on the laboratory-sized padder. This fabric contained twice as much nitrogen as had been obtained with print cloth in a similar run in which 10% 2-aminoethylsulfuric acid and 25% sodium hydroxide were used.

During the course of the work, miscellaneous fabrics of various constructions have been aminized. Due to the complexity of the factors involved in the relationship between fabric structure and degree of aminization, no positive statement can be made on this subject. However, the experiments indicate that a higher degree of aminization is obtained with loosely woven fabrics than with closely woven fabrics.

Aminization with Compounds Related to 2-Aminoethylsulfuric Acid

A number of sulfato compounds related to 2-aminoethylsulfuric acid have been prepared in pure form and reacted with cotton by curing in the presence of sodium hydroxide in order to get some idea of the relative value of these compounds as compared to 2-aminoethylsulfuric acid for introducing amino nitrogen into cotton. The following compounds were found to introduce about 0.2% to 0.4% nitrogen into the cotton: 1,3-diamino-2-sulfato propane sulfate monohydrate, $NH_2CH_2CH_2(OSO_3H)CH_2NH_2 \cdot \frac{1}{2}H_2SO_4 \cdot H_2O$, and the corresponding hydrochloride; sulfatoethyl ethylenediamine hydrochloride, $HOSO_3CH_2CH_2NHCH_2CH_2NH_2 \cdot HCl$; 2(2-sulfatoethyl)pyridine, $C_5H_4NCH_2CH_2OSO_3H$; 3-sulfatopropylamine, $HO_3SOCH_2CH_2CHNH_2$; 2-sulfatoethyl dimethylamine, $(CH_3)_2NCH_2CH_2OSO_3H$; potassium (disulfatoethyl)amine monohydrate, $KO_3SOCH_2CH_2NHCH_2CH_2OSO_3H \cdot H_2O$. The last-mentioned compound apparently acted as a cross-linking reagent when reacted with cotton since the resulting fabric would not disperse in cuprammonium hydroxide solution.

Some related sulfate compounds that reacted very little with cotton when tested by the above technique were: 1-sulfato-2-diethylaminopropane, $(C_2H_5)_2NCH(CH_3)CH_2OSO_3H$; 2-sulfatoethyl-*o*-toluidine, $CH_3C_6H_4NHCH_2CH_2OSO_3H$; and 2-sulfatoethyl aniline, $C_6H_5NHCH_2CH_2OSO_3OH$. The poor reactivity of these compounds may be due to their low solubility in concentrated sodium hydroxide solution.

2-Aminoethylphosphoric acid, $NH_2CH_2CH_2OPO(OH)_2$, and 2-bromoethylsuccinamide, $(CH_2CO)_2NCH_2CH_2Br$, introduced no appreciable amount of nitrogen when cured with cotton in the presence of sodium hydroxide.

Other Methods of Aminization

The method of Stahn [5] was tried in which epichlorohydrin was reacted with cotton in the presence of ethanolamine. Fabric was wetted with epichlorohydrin, placed in a solution containing 17.5% sodium hydroxide and 23.5% ethanolamine, and heated on the steam bath for 5 to 45 min. The resulting fabric contained about 0.2% nitrogen, as indicated by dyeing with Kiton Fast Red. Since both glycerol dichlorohydrins react with sodium hydroxide to form epichlorohydrin, the commercial mixture of the two glycerol dichlorohydrins may be used in place of epichlorohydrin in the above method. For example, cotton fabric was wetted with commercial grade glyceroldichlorohydrin, swabbed with an aqueous solution containing 20% ethanolamine and 20% sodium hydroxide, and heated in an oven for 20 min. at 100°C. Dye tests indicated that the resulting fabric contained about 0.2% nitrogen. Ammonium hydroxide, melamine, or other amino compounds may be used in place of the ethanolamine. When melamine was used some wrinkle-resistance was noted.

Considerable work was done on reacting cotton with the vapor of ethylenimine [1] at temperatures ranging from 60° to 110°C. The resulting cotton contained nitrogen and dyed well with Kiton Fast Red. Much of the ethylenimine was merely polymerized in or on the fiber, since it could be removed by boiling with dilute sodium hydroxide solution or by extracting with dilute acid. However, some nitrogen remained in the cotton after such extractions, indicating that some of the ethylenimine may have combined with the cellulose. It is planned to report this work in more detail in another paper.

Summary

Methods are described for the aminization of cotton in the form of raw stock, sliver, yarn, and fabric by

curing with 2-aminoethylsulfuric acid in the presence of sodium hydroxide. Fabric may be conveniently aminized in a practical manner using standard cotton chemical finishing equipment. Sliver aminized by the process described may be opened, recarded, and converted into yarn. Experiments dealing with the effect of various processing conditions on the aminization of sliver are reported. It is shown that 30% to 35% sodium hydroxide solutions usually give a higher degree of aminization than a 25% solution, and that a 20% solution of 2-aminoethylsulfuric acid under the proper conditions will give almost twice the degree of aminization obtained with a 10% solution. Results of experiments on aminization with a number of compounds related to 2-aminoethylsulfuric acid and some observations on other methods of aminization are reported.

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Chemical and Physical Properties of Aminized Cotton

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MANY PAPERS and patents describe the preparation of amino derivatives of cellulose. Hartmann [9], for example, reported the preparation of aminoalkyl celluloses by reacting the corresponding aminoalkyl halide with cellulose in an alkaline medium. Only recently has it been possible to aminize both yarn and fabric by a method that can be used commercially [16]. This process is carried out merely by moistening cotton cellulose with an aqueous solution containing 2-aminoethylsulfuric acid and sodium hydroxide, heating, washing, and drying the material. Cotton fabric has been aminized by this process on a pilot-plant scale at the Southern Regional Research Laboratory using conventional cotton finishing equipment. The fabrics were padded with a solution of the aminizing reagents, and then cured on dry cans. Excess salts and alkali were washed out on a winch, and the fabric was then dried on a tenter frame.

The chemical structure of this modified cellulose may be represented as follows: cellulose—O—CH_2—CH_2—NH_2. The degree or extent of the substitution may be varied up to about one aminoethoxyl group per 6 glucose units (1.4% N). Concentration of reagents and the curing time and temperature all affect the extent of the reaction. A limiting factor of aminization is that highly aminized cellulose is water-soluble. In the aminization process, the modified cotton is water-rinsed to free it of salts and alkali. During this step if the cotton contains about 1.3% or more of amino nitrogen, it swells, and if it

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is soured with dilute acetic acid, the swelling is so great that fiber structure is likely to be impaired.

The degree of substitution of aminized cotton is low compared to some other useful chemical modifications of cotton, such as partially acetylated cotton [6]; however, these free amino groups, even in very low concentrations, alter the chemical properties of cotton considerably. Aminized cotton may be dyed with acid dyes [8], but this is not the only new chemical property acquired by cotton through aminization. For example, a durable water-repellent fabric can be made by reacting acetyl bromide with the amino group of aminized cotton [17]. These free amino groups convert ordinary cotton into a good anion-exchange material [10], so that aminized fabric will remove anions from solution. This ion-exchange property has been used to make proteins low in ash content [11]. The ion-exchange capacity of aminized fabric can be significantly increased by reacting the modified fabric with ethylenimine [5]. The reactive amino group contributes to the ease of polymerization of ethylenimine with cotton. Considerable flame-resistance can be imparted to aminized cotton by application of a particular type of dye or by reacting it with certain compounds that contain phosphorus or sulfur. Some metals react with aminized cotton to form metal complexes. Aminized cotton can be made rot-resistant by reacting it with 8-hydroxy-quinoline-5-sulfonic acid and then chelating with copper.

The amino groups undergo many of the reactions which are characteristic of aliphatic amines. With nitrous acid the nitrogen is lost. With oxidizing agents like hypochlorite the amine is oxidized, and aminized fabric so treated no longer has the affinity for acid dyes.

The chief purpose of this paper is to compare the chemical properties of aminized cotton with the chemical properties of untreated cotton. Although the physical properties of aminized cotton are not very different from the physical properties of untreated cotton, data will be included on fabric breaking strength, tear strength, flex abrasion, and cuprammonium fluidity.

Dyeing Properties

When aminized cotton is dyed with direct cotton dyes by the techniques generally employed, the aminized cotton shows poor leveling properties due to its increased ability to take up most of these dyes and rapidly exhaust the dye bath. In order to get good level dyeing of aminized cotton, the pH of the dye bath is raised to about 10–12 before the modified cotton is introduced. In this alkaline medium the aminized cotton has only slight affinity for the dye. The pH of the hot dye bath is gradually lowered with a weak acid like acetic acid or an acid-forming material like ethylenechlorohydrin. The rate at which the dye goes on the aminized cotton is associated with the rate of the lowering of pH; therefore, in this manner one can control the rate and levelness of the dyeing.

To illustrate the permanency of direct dyes on aminized cotton, aminized (0.67% N) and untreated cotton were dyed with red and blue Coprantine dyes. These dyes require a copper fixing agent and are known for their lightfastness on cotton. The capacity of aminized fabric for these dyes is considerably greater than that of control cotton. Aminized fabric depleted a 3% dye bath of the red color (RLL) within 25 min., whereas the control did not completely exhaust the dye in 1 hr. A blue Coprantine color (GLL) was put on aminized fabric at 1.5% and 5.0% levels; this same blue color was put on control cotton at 3% level.

A strip of multifiber fabric was attached to samples of aminized and control fabrics which previously had been dyed with 3% red Coprantine dye (RLL). The samples were then laundered by the A.A.T.C.C. Test No. 4 [1], which includes a chlorine bleach. The multifiber fabric attached to the control fabric was stained considerably more than the multifiber fabric attached to the aminized sample. Thus, the aminized cotton retained the dye more tenaciously than the control cotton.

In the Fade-Ometer * there was as much fading of the red Coprantine (RLL) dyed control cotton at 20 hrs. as there was with the aminized cotton at 80 hrs.

Control cotton with 3% blue Coprantine color (GLL) showed slightly more fading in the Fade-Ometer at 80 hrs. than did 1.5% of the same dye on aminized cotton. With 5.0% of the blue dye on aminized cotton only a trace of fading was found after 320 hrs. in the Fade-Ometer. The light-resistance of these dyes on aminized cotton might be due partially to the increased capacity of aminized cotton for these dyes, but this factor alone apparently

* Fade-Ometer Type FDA-R.

does not contribute all of the fastness properties. Some of the results are summarized in Table I.

The dyeing properties of aminized cotton yarn were compared with those of sodium hydroxide-treated and untreated yarn by D. E. Gamble of E. I. du Pont de Nemours and Company. He found that aminized cotton has a noticeably better affinity for direct, vat, sulfur, and developed dyes than either sodium hydroxide-treated cotton or untreated cotton. With the exception of the vat colors, these dyes are slightly more fast to light on aminized cotton. Many of the dyes, especially the direct cotton dyes, were somewhat more fast to washing on aminized cotton than on control yarn. He also found that the dyeing of aminized cotton with cotton dyes requires a shorter time and a lower temperature than usual for application, and also requires less or no salt to exhaust the dye bath.

Tests made by DuPont showed that aminized cotton takes up a number of acid and chrome dyes in a manner similar to wool. The lightfastness of these dyes on both aminized cotton and wool was about equal, but the acid dyes on aminized cotton were less fast to washing than on wool. Although wool and aminized cotton have amino groups which react with acid dyes, apparently wool binds these dyes by an additional mechanism. This fact may have some theoretical interest in relation to the mechanism of the dyeing of wool.

The dye tests made by DuPont also showed that Chromacyl and Neutracyl colors have fair to poor affinity for aminized cotton and that the washfastness of these dyes is poor. Acetate colors dyed aminized cotton to approximately the same low degree that they dyed wool.

Attachment of Flameproofing Agents

Certain dyes contribute flame-resistance to aminized cotton. If aminized fabric is dyed with acid-reacting azo dyes containing at least 1 phosphate or sulfo group to about 7%–10% dye content, a deeply colored fabric having low combustibility is obtained [12]. The flame-resistance is not solely due to the phosphate or sulfo groups in the dye; the nitrogen of the aminized cotton contributes, especially in the presence of these groups. Direct dyes are particularly suitable in that the dye and the flame-resistance property are retained after laundering.

The degree of flame-resistance imparted was determined by igniting the end of a strip of fabric 1 cm. by 7 cm., with the fabric surface vertical, and determining the angular position at which it must be held for the flame to go out. For example, if the strip did not burn in the vertical position when ignited at the bottom, it passed the 180° flame test and had a high degree of flame-resistance. If the flame went out when it was held with the long edge of the strip horizontal and the fabric surface vertical, it passed the 90° flame test and was moderately flame-resistant. If the fabric did not support a flame when held in a vertical position and ignited at the top, it passed the 0° flame test and was slightly flame-resistant. The commercial dyes listed in Table II were put on aminized cotton fabric to about a 10% dye content. The flame-resistance values obtained for the dyed aminized fabrics are given in Table II.

Aminized cotton can also be made flame-resistant by reacting it with heteropoly acids, such as phos-

TABLE I. Copranitine Dyes on Aminized and Control Fabrics

Fabric	Dye color	Dye %	Hours in Fade-Ometer to cause trace fading
Control	Red (RLL)	3	20
Aminized	Red (RLL)	3	80
Control	Blue (GLL)	3	80
Aminized	Blue (GLL)	1.5	80
Aminized	Blue (GLL)	5.0	320

TABLE II. Flame-Resistance of Dyed Aminized Fabrics

Dye*	Color index no.	Flame-resistance (angular degrees)
Direct dyes		
Pontamine Fast Blue 4GL, DuPont (conc., 150%)	533	100
Diazine Black H, National Aniline	401	135
Erie Yellow F, National Aniline	620	90
Pontamine Sky Blue 6BX, DuPont (conc., 150%)	518	90
Acid dyes		
Kiton Fast Red 3 GLL, Ciba		135
Kiton Red S, Ciba	54	110
Kiton Fast Orange G, Ciba	27	110
Amacid Light Yellow 2G, American Aniline	639	110

* The mention of certain products or companies does not in any sense imply an endorsement by the U. S. Dept. of Agriculture over similar products not mentioned.

phomolybdic [15]. When aminized cotton is treated with phosphoric acid, a salt linkage is formed and the flame-resistance will persist after an acidic or neutral wash but not after washing in alkaline tap water. However, if phosphoric acid-treated aminized fabric is placed in a solution of ammonium molybdate, a phosphomolybdate complex is formed [15]. Reduction of the molybdate produced a blue fabric which had flame-resistance sufficient to pass the 135° flame test; this treatment was somewhat resistant to laundering.

Any of the flame-resistant fabrics described above can be made to pass the vertical standard test [2] by applying about 10% poly(triallylphosphate) to the treated fabrics. Poly(triallylphosphate) when used alone does not completely protect cotton fabric from burning.

Aminized cotton can be made permanently flame-resistant by reacting it with tetrakis(hydroxymethyl) phosphonium chloride, $(HOCH_2)_4PCl$. The primary reaction occurs by condensation. Water is split out and a secondary amine is formed; the second hydrogen of the amino group may also react to produce a tertiary amine. The degree of flame-resistance is dependent upon the degree of aminization, since it is the amino groups that combine with the tetrakis compound. With fabric containing about 0.6%–0.7% amino nitrogen, enough flame-resistance is obtained so that the fabric will not support combustion when lighted in a horizontal position (90° flame-resistance). About 1.0% phosphorus is introduced and is stable to an alkali boil. About 95% of the phosphorus is found in the cotton after 2.5 hrs. of boiling in a 1% soap solution containing 0.2% sodium carbonate.

Metal Complexes

Stable metal complexes can easily be made with aminized cotton. Such metals as copper and nickel readily coordinate with amino groups, as do many metals with small amine molecules. Fabric containing 0.8% amino nitrogen stirred for 4 hrs. with 1.0% copper acetate solution produced a blue fabric containing 1.25% copper. The complexed copper can be reduced in the fabric to metallic copper with a dilute alkaline solution of sodium hydrosulfite ($Na_2S_2O_4$). Mild oxidizing agents like tap water will oxidize the reduced form. The copper can be repeatedly reduced and oxidized without substantial loss of the metal. Certain amine resins complexed with copper are employed to remove oxygen from water [13]. It seems that copper complexed with aminized fabric might offer some advantages, such as ease of manipulation, over the resins in removing oxygen from water.

TABLE III. ROT-RESISTANCE OF COPPER-CHELATED FABRIC

	Breaking strength (lbs.) Days in soil bed:					
Fabric	0	7	14	24	33	41
Untreated	72.8	3.9				
Aminized	60.0	30.0	5.7			
Aminized-chelated	51.4	42.1	26.1	16.8	17.5	15.0

Another way of getting metals into cotton is to react a chelating compound with the aminized cotton. The sulfonic acid group of 8-hydroxyquinoline-5-sulfonic acid reacts rapidly to give a fabric which will form a chelate with many cations. When chelated with zinc, a light yellow fabric is obtained which possesses a bright yellow color in ultraviolet light. Copper-chelated fabric is green and fluoresces dark red in ultraviolet light. Fabric containing chelated copper has good rot-resistance.

Chelated fabric containing 0.6% copper was made by stirring aminized fabric (0.8% N) for 15 min. in hot 1% aqueous solution of 8-hydroxyquinoline-5-sulfonic acid containing 0.5% acetic acid. After this fabric was thoroughly rinsed it was reacted for 2 min. in a hot 5% copper acetate solution containing 0.5% acetic acid. Rot-resistance values of the fabric determined by the A.S.T.M. soil burial test [3] are reported in Table III.

It is apparent that aminized fabric itself offered some resistance to microorganisms, and the aminized cotton fabric chelated with copper lasted much longer than the untreated fabric. When the chelated fabric was laundered in accordance with A.A.T.C.C. Test No. 4 [1] and then placed in the soil bed for 36 days, it had a breaking strength of only 1 lb. It is obvious that the rot-resistance of the chelated fabric did not withstand severe laundering; however, it stood tap-water washing. For uses where laundering is not a critical factor and rot-resistance is important the chelated fabric may be valuable.

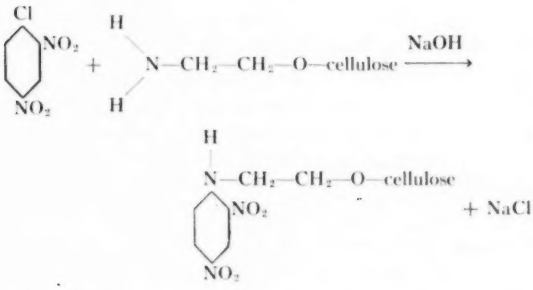
Reaction with Nitrochlorobenzenes

Chloro-substituted nitrobenzenes having the chlorine either *ortho* or *para* to a nitro group react with aminized cotton to form nitro-substituted aniline

TABLE IV. REACTION OF AMINIZED COTTON AND CONTROL COTTON WITH NITROCHLOROBENZENES

Cotton	Nitro compound reacted	Conc. of nitro compound (%)	Reaction time (min.)	N introduced (%)
Aminized	Dinitro	1.0	10	0.17
Aminized	Dinitro	1.0	20	0.20
Aminized	Dinitro	2.0	10	0.18
Control	Dinitro	2.0	20	0.0
Aminized	Trinitro	1.0	10	0.02
Aminized	Trinitro	2.0	7.5	0.62
Aminized	Trinitro	2.0	35	0.97
Control	Trinitro	2.0	35	0.0

ethoxyl celluloses:



These nitro groups can be reduced, diazotized, and coupled with phenols to give numerous colored products which resist ordinary laundry treatments. The coupled phenol can be cleaved by reduction and then a second phenol can be coupled by diazotizing the aromatic amine.

These same nitrochlorobenzenes were introduced into the cellulose molecule a number of years ago [7], but the method of doing it was rather drastic. The cellulose was first swelled by soaking several hours in 10% caustic soda; thereafter the alkali was removed by washing; then the moist fibers were treated at 90°–95°C for several hours with nitrochlorobenzene in the presence of lithium carbonate. A less drastic method [14] was described later. Even this method required refluxing for 8 to 10 hrs. in ethanol.

The present reaction requires that the aminized cotton be agitated for 5 to 10 min. in a hot (70°–90°C) aqueous bath consisting of 1% to 2% of sodium hydroxide and 1% to 2% of nitrochlorobenzene. Under these conditions 2,4-dinitrochlorobenzene and 2,4,6-trinitrochlorobenzene reacted with aminized cotton, but with ordinary cotton only a trace of nitrogen was introduced (Table IV). The dinitro compound reacted more uniformly than the trinitro compound and was more easily reduced after it was attached to the aminized cotton.

The physical properties of moderately aminized cotton (0.3%–0.8% N) are not very different from those of ordinary cotton. Generally, a slight stiffness is its most pronounced physical feature. This property is increasingly more pronounced as the degree of aminization increases. Aminized fabric is more easily soiled and retains the soil more tenaceously than control cotton [18]. Aminized fabric (0.67% N) had a cuprammonium fluidity of 15.4 rhes, whereas the fluidity of a sodium hydroxide-treated control fabric was 11.4 rhes and that of an untreated control fabric was 2.94 rhes. Tear strength and breaking strength are about the same as that of ordinary cotton, but aminized cotton fabrics have noticeably better abrasion-resistance (Table V).

Summary

The chemical reactions of aminized cotton are quite different from those of untreated cotton.

TABLE V. PHYSICAL PROPERTIES* OF AMINIZED COTTON FABRICS

Fabric	Breaking strength† Strip (lbs.)	Breaking strength† Grab (lbs.)	Trapezoid tear† (lbs.)	Flex abrasion† (cycles)
Aminized (0.7% N) 2-oz. lawn	27.5	33.2	2.9	1651
Control 2-oz. lawn	30.0	32.0	3.3	716
NaOH-treated 2-oz. lawn	32.4	40.5	3.6	2786
Aminized (0.67% N) 80 × 80 print cloth	43.5‡		3.3	369
Control 80 × 80 print cloth	49.3‡		3.4	251
NaOH-treated 80 × 80 print cloth	40.8‡		3.5	969

* Determined by A.S.T.M. methods [4].
† Average of warp and filling.
‡ Warp only.

Aminized cotton takes on most cotton dyes very rapidly, and some of these, especially direct dyes, are more resistant to light and laundering on aminized than on untreated cotton. Although acid dyes are readily taken by aminized cotton, they are not fast to laundering. Combustibility of aminized cotton can be reduced either by application of dyes containing a phosphate or a sulfo radical or by reacting the amino groups with tetrakis(hydroxymethyl)phosphonium chloride. Certain metals react with the amino groups to form metal complexes which have oxygen-exchange properties. Aminized fabric can be given considerable rot-resistance by reacting with 8-hydroxyquinoline-5-sulfonic acid and then chelating with copper. Aminized cotton reacts with *ortho*- and *para*-nitrochlorobenzenes in dilute solutions.

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Tight-Lock of Cotton, Associated Fungi and pH Values in South Carolina in 1952

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Contribution from the South Carolina Agricultural Experiment Station, Clemson, South Carolina

THE possible adverse effect of microbial tight-lock of seed cotton on the spinning quality of the fibers derived from such seed cotton [2] provided the incentive for a field survey to ascertain the prevalence of such tight-lock in South Carolina in 1952. Samples of tight-lock collected during August and September were used to ascertain the infesting fungi and the associated pH values. The data reported in this paper were derived from bolls and locks which showed no sign of insect injury. It was thought desirable to confine this study to tight-lock directly induced by fungi, although there is no reason to presume that the inclusion of abnormal locks from bolls that had been injured by insects would have changed the relative abundance of the several fungi as reported in Table I, except possibly for those that produced a dark discoloration of the seed cotton.

The selected locks were grouped into two empirical categories: (*a*) dense tight-lock, or locks that were relatively small, mostly discolored, and not likely to be picked as undeteriorated seed cotton; and (*b*) moderate tight-lock, or full-sized locks that were approximately the size of normal locks before fluffing and were usually only slightly if at all discolored. Most of the latter were obtained from normally dehisced bolls. The dense tight-locks were also obtained from open bolls, but the latter had not always reached their full size and the carpels had not always separated so widely as those of normal bolls. The results reported are based on the examination of approximately 120 tight-lock bolls of class (*a*) and 200 of class (*b*), as gathered at random throughout the state.

Previous to the examination of locks for infesting fungi, they were held on moist paper toweling in a damp chamber at 20°–25°C for 1 to 2 days, or until the fungi on the locks had developed sufficiently to permit their identification. The locks were then dried at room temperature and their pH values ascertained within the next 3 days. The extract for the determination was prepared by kneading each lock in about 10 ml. of distilled water to which a drop of a wetting agent * had been added. The lock was held in the distilled water for 3 min. before the pH was ascertained colorimetrically with an appropriate set of indicators on a white porcelain spot plate by comparing the color of the lock extract with that of a solution of known pH.

The fungus recorded as present in a lock was not necessarily the only one that might have been found if another technique had been used. It is thought that the fungus recorded as being present was the one primarily responsible for the tight-lock condition, since it was the first fungus to fruit abundantly and since more than one fungus was present in only about 10% of the locks. A nonsporulating fungus would have been overlooked, unless its mycelium was readily distinguished from that of the sporulating fungus. The presence or absence of bacteria also is not noted, since most locks infested by fungi were also to some extent infested by bacteria.

Fungi and Associated pH Values

Fusarium spp. were the most prevalent fungi on the moderately tight-lock seed cotton (Table I), with *Alternaria* spp. forming the next largest group. Species of these two genera and *Diplodia gossypina* Cke. were the predominating fungi on the densely tight-lock seed cotton. *Fusarium moniliforme* Shel. was found on only 3% of the locks, or about 10% of those infested by *Fusarium* spp. Only a small percentage of the locks was infested by *Colletotrichum gossypii* South. The low incidence of infestation by this fungus may have been associated with the generally dry weather throughout the growing season.

* NNO, Atlas Powder Co.

TABLE I. PERCENTAGES OF TIGHT-LOCK SEED COTTON INFESTED BY SEVERAL FUNGI AND ASSOCIATED pH VALUES

	Degree of tight-lock					
	Moderate			Dense		
Infesting fungi	%	Range pH	Mean pH	%	Range pH	Mean pH
Fusarium spp.	40	7.2–9.6	8.9	26	7.0–9.6	8.1
Alternaria spp.	23	7.4–9.6	8.8	29	7.2–9.2	8.0
Diplodia gossypina	8	6.8–9.6	7.9	27	5.7–8.0	6.9
Colletotrichum gossypii	10	7.6–9.6	8.8	4	7.2–8.4	7.8
Nigrospora sp.	5	7.4–9.0	7.7			
Rhizoctonia sp.	3	7.0–7.6	7.3			
Macrophominia sp.	2	7.4	7.4			
Streptomyces sp.				4	7.2–8.4	7.5
Cladosporium sp.	1	8.6–9.6	9.2			
Two fungi*	8	7.6–9.6	8.6	10	7.2–8.4	7.8

* Locks infested by two species of fungi, largely *Fusarium* and *Alternaria* spp.

The other fungi observed of the genera *Nigrospora, Rhizoctonia, Macrophominia, Streptomyces,* and *Cladosporium* are probably not economically important factors as a cause of tight-lock, except for a *Cladosporium* sp. which has been found more abundantly in other collections of seed cotton [5].

The range in pH values for the seed cotton infested by the several fungi was much the same (Table I). This is not unexpected, since the pH has been shown [5] to be related to the chemical changes produced in the fibers by the fungi. The mean pH values for seed cottons infested by the several fungi, however, were quite different. Thus, the mean for the moderately tight-lock seed cotton infested by *Fusarium* spp. was 8.9, and for those infested by *D. gossypina* 7.9; for the dense tight-locks, the corresponding pH values were 8.1 and 6.9. The frequency distributions of the pH values also showed greater differences than the ranges. Thus, although the range of pH values for the *Fusarium*-infested locks was 7.0 to 9.6, one-half of the values were 9.0 or greater; for the *Alternaria*-infested locks more than 66% of the locks had a pH greater than 8.0; for those infested by *D. gossypina* less than 15% had a pH greater than 7.5. This tendency of the seed cotton infested by *D. gossypina* to have distinctly lower pH values than those infested by other fungi has already been noted [5]. The number of observations for the other fungi was not large enough for similar comparisons.

The distribution of the pH values among selected ranges of the tight-lock samples and those of normally fluffed seed cotton from the same fields is shown in Table II. Only 40% of the tight-lock samples were below pH 8; about one-third of these were locks that were blackened as the result of infestation by *D. gossypina.* In contrast, 87% of the normally fluffed samples had a pH of less than 8.

TABLE II. PERCENTAGES OF pH VALUES IN SELECTED RANGES FOR TIGHT-LOCK AND NORMALLY FLUFFED SEED COTTON COLLECTED IN 1951, AND ALSO FOR REGULARLY HARVESTED SEED COTTON AS DELIVERED TO GINS IN 1951 AND 1952

Kind of seed cotton	No. of samples	Percentages in selected pH ranges: 6.5–6.9	7.0–7.4	7.5–7.9	8.0–8.4	8.5–8.9	9.0–9.6
Tight-lock	320	7	20	13	16	12	32
Normal	100	0	45	42	11	0	2
Gins, 1952	66	0	9	50	26	10	5
Gins, 1951	71	3	38	24	24	7	4

Comparable samples of harvested seed cotton were not obtained from the same fields as those from which the normally fluffed and tight-lock seed cotton were obtained; but the pH values were obtained for 66 randomly selected lots of seed cotton as delivered to various gins before Oct. 1, 1952. Of these, 59% had a pH of less than 8, and 41% a pH greater than 8. The corresponding values for 71 samples examined in 1951 were 65% and 35%. Thus, in these collections the pH values were generally the lowest for normally fluffed seed cotton, and were highest for tight-lock seed cotton; while those for seed cotton as delivered at the gins were intermediate, the latter values apparently being influenced by the amount of tight-lock seed cotton mixed with that which had fluffed normally.

The effect of the action of the fungi during periods of high humidity is indicated by limited examinations of the seed cotton of unopened bolls and of unweathered and artificially weathered seed cotton. Locks of seed cotton obtained from mature but unopened bolls that were collected at 2 P.M. on a partly cloudy day and immediately brought to laboratory and tested had a pH of 5.6. Similar locks of seed cotton when dried without artificial heat in the laboratory at low humidity gradually increased their pH to 6.2–6.4. In contrast, the pH of seed cotton of bolls about to dehisce, as shown by the immediate splitting of the bolls when pressure was applied, and of bolls in which the carpels had separated only slightly ranged from 6.4 to 7.2, with the average approximating the lower value. These values did not change or changed only slightly when the bolls were dried

in the laboratory. When exposed to high humidity in the laboratory, the pH values for most locks increased to a maximum of 8.8 after 3 days. Similar results have been reported previously [5].

Discussion

The fungi reported in this paper as associated with tight-lock are essentially those reported previously [1, 3, 4, 5]. The important differences are in the relative prevalence of the several fungi. Such differences are to be expected, since it may be presumed that fungi infesting seed cotton will vary from field to field and from season to season according to the humidity to which the maturing bolls are subjected [4]. The rainfall had been unusually low throughout most of the growing season in 1952; and the plants in the average cotton field were typically small and the ground was only partially shaded. Consequently, angular leaf spot as well as the anthracnose and *Diplodia* boll rots were prevalent only in the small percentage of fields with large, densely foliated plants. Similar studies will have to be carried out over several years before a definite conclusion can be drawn concerning the relative importance of the several fungi as a cause of the tight-lock of seed cotton.

The characteristic blackish discolorations produced by the anthracnose fungus and *D. gossypina* have been described by Marsh *et al.* [4]. Similar discolorations, although without the typical pycnidial stroma of *Diplodia*, were produced by *Macrophominia* and *Nigrospora* spp. The latter fungus has been previouly recorded as a cause of microbial tight-lock [4]. The typical discoloration produced by the *Alternaria* spp. was a dark olive gray, but the degree of discoloration varied from slight to very dark. The discoloration produced by the *Fusarium* spp. was similarly variable, and ranged from slightly yellow, tan, pink, to dark brown. The fibers of the brownish locks, even when only partially tight-lock, were often soft and fragile, which would seem to indicate severe destruction of the fiber walls by the infesting fungus or fungi. Field estimates indicated a definite gray or blackish discoloration of about one-fourth of the microbial tight-locks. In contrast, the seed cotton of most of the bolls that showed insect injury was distinctly discolored.

Conclusions

The fungi associated with tight-lock of seed cotton in South Carolina in 1952, in order of descending prevalence, were *Fusarium* spp., *Alternaria* spp., *Diplodia gossypina*, and *Colletotrichum gossypii*. *Diplodia* was relatively more abundant on small, dense, and black locks than on the larger tight-locks. The pH of the locks varied with the infesting fungi. Those infested by *D. gossypina* had a mean value of 7.9 or lower; while these infested by *Alternaria* and by *Fusarium* species had a mean value between 8.0 and 8.9, respectively. The pH values of normally fluffed seed cotton were generally below 8, while the average pH value of seed cotton as delivered to the gins was higher.

Only 13% of the samples of normally fluffed seed cotton as collected in the field in 1952 had a pH value greater than 8, in contrast to samples of seed cotton as delivered to the gins, of which 41% had a pH value of 8 or higher in 1952 and 35% in 1951.

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Some Properties of Serges Made from Blends of Wool with Acrylic Type Synthetics*

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Introduction

The introduction of many types of new fibers in the past decade has increased the variety of possible combinations in blending to a very high degree. The traditional sequence in evaluation of fabrics involving the steps of fabric design, preparation, and testing now has become increasingly slow and expensive. This has led to an appreciation for the need of better organized approaches to develop the basic principles needed to relate the behavior of the fabric to the properties of the fiber and yarn, to the construction variables, and to finishing procedures.

As a large-scale consumer of textiles, the military services are vitally concerned with the potentialities of blending in terms of conservation, of lowered costs, and of enhanced functionality. As part of an overall program of research on blends initiated by the Army Quartermaster Corps, an investigation of the effects of blending as related to the warmth and comfort characteristics of fabrics has been undertaken. The present paper describes some preliminary results of a laboratory study of fabrics containing wool blended with varying amounts of the synthetic fibers based on acrylonitrile—Orlon, Dynel, and Acrilan. It will be emphasized throughout the discussion that the results reported here are based on the particular fabrics examined, which, while intended to be as representative as possible of the results of blending, are nevertheless merely one set of trials in this direction. The emphasis is placed on the basic features of fabric structure and performance illustrated by these particular fabrics and on the indications as to how desired fabric characteristics may be achieved in blended fabrics. As will be seen, factors of yarn and fabric structure and finishing operations applied are certainly equal in importance to the factors of fiber composition.

* This work constitutes a part of the Army Quartermaster program of research on warmth and comfort of military fabrics performed under contract QM 564.

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Fabric Design and Construction

Most of the work reported here was done with a series of dyed serge fabrics of the type used in Army uniforms [10]. The fabrics were made on a sufficiently large scale so that the results would be representative of mill production. Since these garments may be laundered in the field, measurements of fabric properties were made after the equivalent of three 19-min. field launderings. The fabric constructions are given in Table I as determined from the fabrics after laundering. It will be noted that while the same lot of wool was used for blending, a different all-wool control fabric was made with each blend type since manufacturing with each synthetic fiber took place at different times; it was believed that this procedure permitted a more appropriate comparison of the blends with the all-wool fabric. Three-denier Orlon and Acrilan were used in preparing the blends. In the case of Dynel, 20% of the synthetic was 6 den.; it will be shown that the presence of the coarse fibers in this group had a significant effect on some of the characteristics of the blended fabrics.

The choice that was made in the experimental design was to maintain the fabric texture (picks and ends) constant, and fairly good control of this variable was maintained. The yarn number specified was deliberately increased as the synthetic content was increased with the purpose of maintaining the yarn diameter and "cover" constant. The thinking at the planning stage was concerned with avoiding an increase in yarn diameter that could result with increasing content of the low-density fibers if identical yarn sizes were used throughout. The plan was successfully accomplished except in the case of sample 15 (all Dynel) where the yarns were too heavy; hence, this fabric is appreciably heavier than any other in the group. In all other cases, the trend of decreasing weight and yarn number with decreasing wool content is clearly marked. It is noted at this point that the all-Dynel fabric (no. 15) had a glazed appearance as if pressed unduly hard or at too high

TABLE I. CONSTRUCTION DETAILS OF SERGES

Sample No.	Nominal fiber content* Wool (%)	Other (%)	Texture Warp (ends/in.)	Filling (picks/in.)	Worsted yarn No. Warp	Filling	Weight (oz./yd.²)
42	100	0	68	62	2/23	2/26	12.4
8	85	15 Dynel	70	56	2/24	2/25	12.7
12	70	30 Dynel	68	54	2/24	2/27	11.7
14	50	50 Dynel	69	55	2/28	2/28	11.6
15	0	100 Dynel	69	57	2/24	2/26	13.8
51	100	0	69	59	2/25	2/26	12.1
53	85	15 Acrilan	68	55	2/26	2/27	11.4
54	70	30 Acrilan	69	58	2/25	2/27	10.7
55	50	50 Acrilan	70	57	2/30	2/29	9.7
52	0	100 Acrilan	71	52	2/29	2/29	9.5
17	100	0	69	62	2/26	2/25	12.3
23	85	15 Orlon	71	59	2/27	2/26	11.6
26	70	30 Orlon	69	56	2/27	2/27	11.4
28	50	50 Orlon	70	58	2/30	2/31	10.8
20	0	100 Orlon	69	58	2/32	2/32	9.5

* The wool was 58/60's grade. The Acrilan and Orlon fibers were 3-den., 4-in. staple; the Dynel was a blend of 80% 3 den. and 20% 6 den., both 4-in. staple.

a temperature, and hence the sample differed from the other samples in this respect as well. This sample exhibited anomalous behavior with respect to several of the properties studied, and is not considered to be strictly comparable to the other fabrics in the group.

Experimental Results

Properties Related to Warmth

The fabrics were measured for thermal resistance using a modified two-plate Cenco Fitch apparatus [7]. In brief, this consists in placing a specimen between two metal plates, a source at 50°C and a receiver at room temperature, and determining the change of temperature of the receiver with time. The plates may be separated by known distances, and hence the thermal properties of the fabric may be determined at thicknesses corresponding to known pressures on the cloth. Another advantage of this technique is that the contribution of the fabric itself to the thermal resistance is determined in the absence of the associated still air layers; the latter may make a greater contribution to the over-all insulation [4, 14] than the fabric (particularly with thin fabrics), and this may obscure the effect due to the fabric alone.

The intrinsic thermal resistance of the fabrics determined at thicknesses corresponding to pressures of 0.002 lb./in.² and of 1.0 lb./in.² are shown in Table II.

With the Acrilan and Orlon blends, the samples exhibit a tendency to become thinner as the synthetic content is increased. The fabric containing 15% Acrilan is slightly thicker than the all-wool control, but that containing 30% is somewhat thinner; in the Orlon series the sample containing only 15% synthetic is already thinner than the wool. The presence of a greater fraction of coarse fibers in the Dynel series is believed to result in the maintenance of fabric thickness, even when the blend contains as much as 50% synthetic; this would follow if the coarse fibers tend to spin to the outside of the yarn and, from the resistance of these coarser, stiffer fibers, to be aligned into the body of the yarn.

The results of the thermal measurements are in agreement with those of many other studies [12, 14, 15, 18] in that the insulating value is proportional to the thickness of the cloth. Thus, the thermal resistance per inch of thickness (specific resistance) is shown to be constant—1.9 to 2.1°C m.²sec./cal. The only cases in which the specific resistance is lower are those for the all-synthetic fabrics at higher pressures. This is believed to be associated with the high bulk density of these fabrics and possibly the inherently greater conductance of the fiber substance compared with wool; this effect will be discussed elsewhere.

A comparison among the all-wool samples is of interest. It should be noted that although these fabrics were substantially identical in construction details

TABLE II. THERMAL RESISTANCE AND THICKNESS OF BLENDED SERGES

Sample No.	Nominal fiber composition Wool (%)	Other (%)	Thickness At 0.002 lb./in.² (mils)	Thickness At 1.0 lb./in.² (mils)	Thermal resistance At 0.002 lb./in.² Intrinsic (°C sec. m.²/cal.)	At 0.002 lb./in.² Specific (°C sec. m.²/cal. in.)	At 1.0 lb./in.² Intrinsic (°C sec. m.²/cal.)	At 1.0 lb./in.² Specific (°C sec. m.²/cal. in.)
42	100	0	97	41	0.198	2.0	0.081	2.0
8	85	15 Dynel	97	45	.182	1.9	.090	2.0
12	70	30 Dynel	99	46	.185	1.9	.093	2.0
14	50	50 Dynel	94	43	.180	1.9	.083	1.9
15	0	100 Dynel	48	39	.090	1.9	.066	1.7
51	100	0	87	38	.173	2.0	.077	2.0
53	85	15 Acrilan	93	39	.200	2.1	.078	2.0
54	70	30 Acrilan	81	35	.164	2.0	.065	1.9
55	50	50 Acrilan	68	32	.142	2.1	.060	1.9
52	0	100 Acrilan	41	28	.083	2.0	.049	1.7
17	100	0	103	41	.198	1.9	.077	1.9
23	85	15 Orlon	84	38	.172	2.0	.072	1.9
26	70	30 Orlon	86	38	.172	2.0	.071	1.9
28	50	50 Orlon	74	34	.148	2.0	.063	1.9
20	0	100 Orlon	38	28	.076	2.0	.048	1.7

(Table I), sample 51 was appreciably thinner than the other all-wool samples and the thermal resistance at low pressure was correspondingly about 15% lower. It will be shown that the differences in thickness among these fabrics may be explained by differences in surface hairiness. For the present, however, it must be made clear that differences among fabrics with respect to thickness or thermal insulating properties may be interpreted as a consequence of the kind of yarn or fabric that is manufactured rather than of the particular percentage of synthetic chosen to prepare the blend.

Surface Hairiness

If comparisons are made of the handle of the wool serges with those made largely or entirely of synthetic fibers, the latter are seen to be less hairy. This factor may be appreciated in a quantitative way from the differences in thickness observed at 0.002 and at 1.0 lb./in.² (see Table II); especially in the blends containing Orlon and Acrilan the total compression decreases in proportion to the decrease in wool content.

The surface hairiness was also evaluated by a rate of cooling test developed in these test laboratories [9]. The method, in essence, involves measurement of the rate of cooling of a small copper disc initially heated to 15°C above ambient temperature when a small fabric specimen is placed in contact with it.

The data given in Table III show the $t_{\frac{1}{2}}$ values, the time required to cool the disc 7.5°C, and the values of nk/l, a parameter calculated from the slope of the cooling curves and related to the number of surface fibers, n, the conductance of the fiber substance, k, and the mean length of the surface hairs, l. The time for cooling is long for fuzzy fabrics which make poor contact with the heated disc and conversely rapid for smooth fabrics; the surface fiber conductance, nk/l, is an inverse function of $t_{\frac{1}{2}}$, and hence small values of the former are associated with hairy fabrics.

The data indicate that all of the blends containing 70% or more of wool are relatively fuzzy and approximately similar to one another. The all-synthetic serges are smooth and nonhairy. The 50/50 blends are intermediate in character in the cases of fabrics made with Orlon and with Acrilan. The Dynel blend, perhaps because of its content of higher denier fibers already noted, tends to be of the more hairy type in this instance. These appear to relate to the thickness data in Table II. Thus, the thickest group of fabrics are the fuzziest, and the thinnest samples are the smoothest. The result suggests that the difference in thickness between fuzzy and smooth fabrics is due mainly to the length and density of the fuzz fibers on the fabric surface. The role of fuzziness (equated to thickness) in thermal resistance has been noted in a previous section, and its place in resistance to wetting will be considered subsequently.

TABLE III. SURFACE HAIRINESS OF SERGES AS ESTIMATED BY A RATE OF COOLING METHOD

Sample No.	Nominal fiber composition: Wool (%)	Nominal fiber composition: Other (%)	Time to cool 7.5°C (t_4) (sec.)	Specific conductance of the surface fibers (nk/l)* (cal./°C cm.² sec.)
42	100	0	71	8.2×10^{-4}
8	85	15 Dynel	74	7.6
12	70	30 Dynel	76	7.2
14	50	50 Dynel	71	8.0
15	0	100 Dynel	53	13.2
51	100	0	68	8.9
53	85	15 Acrilan	71	8.0
54	70	30 Acrilan	65	9.3
55	50	50 Acrilan	58	10.9
52	0	100 Acrilan	49	14.4
17	100	0	73	7.7
23	85	15 Orlon	72	8.1
26	70	30 Orlon	70	8.4
28	50	50 Orlon	69	8.3
20	0	100 Orlon	49	14.2

* n is the number of surface fibers per unit area, k is the conductance of the fiber substance, and l is the mean length of the surface hairs.

From another point of view, the rate of cooling method may be said to evaluate directly the coolness-to-touch aspect of fabric handle. In terms of this criterion, garments made of the smooth serges (all synthetic) would be expected to give a cooler sensation immediately on donning as compared with the relatively warm feel that might be expected with samples containing more than 50% wool. Hoffman and Beste [8] have discussed this question of contact warmth in terms of the heat capacity and the thermal conductivity of the fiber substance and of the area of contact between fabric and skin. While data on the former two properties are not available, it seems probable that the area of contact is of major importance for the present fabrics and may be used to account for the results observed.

Wicking Properties

It has been observed [6] that in general the use of synthetic fibers in blending increases the ease of wetting and the wicking rate of fabrics. While the physiological importance of this phenomenon—*e.g.*, in transport of perspiration and water vapor from the skin—remains to be established, it was considered desirable nonetheless to evaluate this series of serges with respect to wicking behavior because of the relation of this property to intrinsic water-repellency and because of the potential importance of water-transport mechanisms in the wet thermal studies now in progress.

TABLE IV. DROP ABSORPTION AND WICKING OF BLENDED SERGES

Sample No.	Nominal fiber composition: Wool (%)	Nominal fiber composition: Other (%)	Drop absorption time (0.2 ml.) (sec.)	Longitudinal wicking (sec. per 1-in. rise)
42	100	—	26000+	20000+
8	85	15 Dynel	26000+	5000
12	70	30 Dynel	26000+	1000
14	50	50 Dynel	5000	600
15	0	100 Dynel	200	500
51	100	—	26000+	30000+
53	85	15 Acrilan	20000+	9000
54	70	30 Acrilan	6000	6000
55	50	50 Acrilan	2000	6000
52	0	100 Acrilan	200	1000
17	100	—	29000+	49000+
23	85	15 Orlon	20000+	35000+
26	70	30 Orlon	10000	4000
28	50	50 Orlon	1500	1500
20	0	100 Orlon	1000	4000

Two types of measurements were conducted: (*1*) drop absorption, in which 0.2 ml. of water is placed on the fabric surface and the time observed to complete disappearance of free liquid; and (*2*) longitudinal wicking, in which a warp strip (1 in. wide) is immersed as a wick in a vertical position in water and the time required for the liquid to rise a height of 1 in. determined. The results are shown in Table IV.

The all-wool controls and the blends containing only 15% synthetic show high resistance to wetting and wick the slowest. At the opposite end of the wicking scale, the all synthetics are easier to wet and wick the most readily, with the blends containing 50%–70% wool being intermediate between these extremes. The ability of a fabric surface to be wet has been shown to depend on the surface smoothness [5, 16]. The results for the present fabrics are consistent with the effect, the wicking and drop absorption rates varying inversely with fabric hairiness. It is intended to study the wetting characteristics of the fiber substance as such—*i.e.*, contact angle with water—to determine whether the nature of the fiber surface is a factor in wetting or whether the main effect is explained by capillarity alone.

The interpretation of these results in terms of the

use situation is difficult since a practical scale of values has not yet been developed. There is no question that the use of synthetics in this series increases the wicking tendency. However, if it is assumed that the drop absorption time is an index of resistance to wetting of the fabric (as in a garment under a leaky raincoat seam), the times involved are moderately long—on the order of ½ to 1 hr. or more for blends containing up to 50% synthetic fiber. If the longitudinal height of rise data are thought to simulate the wicking in another type of practical situation (corresponding to immersion of the trouser leg bottom in water), then even under the worst conditions the results in Table IV would predict a height of rise of 1 in. in approximately 10 min. for the present construction.

Fabric Stiffness, Crease Recovery, and Muss-Resistance

This group of properties was used to evaluate these serges with respect to some appearance characteristics. The bending length was determined by a modification of Peirce's cantilever method [1]; the flexural rigidity was also calculated from these measurements. The bending length is an index of the stiffness in drape, whereas the flexural rigidity reflects differences in resistance to hand-bending.

The crease recovery tests were made with the Monsanto tester [11] by two procedures: (*a*) loading for 5 min. at 65% R.H. and measuring recovery after 5 min.; (*b*) loading for 15 min. between moist blotters and measuring recovery after 5 min.

Muss-resistance was evaluated by a procedure developed in these laboratories. Fabric specimens were placed into a tumble jar containing moist sponges and rubber stoppers to provide mechanical action. After tumbling for 20 min., the specimens were removed and visually examined for mussing immediately, after 5 min. of rest, and after 1 hr. of rest. The results after 5 min. are given in Table V, the relative muss-resistance being arbitrarily classified as good, moderate, or poor; this classification only compares the samples with one another and does not refer to any absolute standard of mussing. The stiffness and the crease recovery data are also given in Table V.

With two notable exceptions the bending lengths of the serges are similar; the all-Dynel sample no. 15 is markedly stiffer and the all-Orlon sample no. 20 is lower in bending length than the other materials. Since the weight of the fabric enters into the calculation of flexural rigidity, the latter values appear to correlate with the values of the weight per square yard shown in Table I. The stiffness of sample 15 is believed to result from the excessive unit weight of the fabric, whereas the limpness of sample 20 may follow from the high yarn number—*i.e.*, low yarn diameter. In general, it should be noted that differences in the stiffness behavior are probably influenced to a much greater degree by structural effects than by any differences in fiber type or blend.

TABLE V. STIFFNESS, CREASE RECOVERY, AND MUSS-RESISTANCE OF BLENDED SERGES

Sample No.	Nominal fiber composition Wool (%)	Other (%)	Mean bending length (cm.)	Mean flexural rigidity (g. cm.)	Monsanto crease recovery Dry (%)	Moist (%)	Relative muss-resistance
42	100	—	2.3	0.47	86	65	moderate
8	85	15 Dynel	2.2	.46	83	61	good
12	70	30 Dynel	2.1	.37	80	61	good
14	50	50 Dynel	2.1	.39	79	56	good
15	0	100 Dynel	2.6	.86	75	71	good
51	100	—	2.2	.45	86	64	moderate
53	85	15 Acrilan	2.1	.37	84	60	good
54	70	30 Acrilan	2.1	.32	83	57	good
55	50	50 Acrilan	2.2	.33	78	57	good
52	0	100 Acrilan	2.0	.28	66	60	good
17	100	—	2.2	.43	88	63	moderate
23	85	15 Orlon	2.1	.37	84	62	good
26	70	30 Orlon	2.0	.33	82	59	good
28	50	50 Orlon	2.0	.29	78	54	good
20	0	100 Orlon	1.8	.19	73	67	moderate to good

The dry crease recovery data indicate that for these materials the addition of increasing amounts of synthetic fiber tends to lower the crease recovery somewhat, as measured in this test. The unduly low value for sample no. 52 (all Acrilan) appears to be anomalous, although it is noted that this fabric is made with fewer picks than any other in the group. The crease recovery of the moist fabrics containing wool also tend to decrease with decreasing wool content and weight. Moisture affects the crease recovery of the all-synthetic samples to a smaller extent than the all-wool fabrics or any of the blends. This is associated with the higher fiber stiffness of these synthetics in the wet state compared to wool. In the case of Dynel and Orlon, the all-synthetic samples show more recovery when moist than any of the corresponding blends or wool controls.

The generalization which emerges from the visual evaluation of muss-resistance is that the addition of synthetics of low regain to the blend enhances the muss-resistance (moist) considerably. The all-Orlon fabric gave somewhat variable results in this test; its tendency to relatively low muss-resistance may be due to the soft, limp construction as shown by the low flexural rigidity.

Compression Measurements

Compression measurements were made on these samples using the Schiefer compressometer [13]. An empirical means has been described [2] for calculating an "equation of state" for fabrics, $t = a + b/(p + .05)$, by means of which the thickness, t, may be satisfactorily estimated at any pressure, p, in the range 0.002 to 2.0 lbs./in.^{2} by means of the "constants" a and b. The b value is believed to characterize the fabric with respect to the hairiness of its surface and to its compressibility at low pressures. The calculated values of a and b are shown in Table VI. In addition, Table VI lists the results of thickness recovery from compression to 0.1 lb./in.^{2} and unloading to 0.002 lb./in.^{2}

The b values in Table VI are indicative of the decreasing surface fuzziness as the Acrilan or Orlon content becomes large. This result is consistent with the evidence from the rate of cooling measurements discussed previously. The thickness recovery values suggest that percentagewise the fabric returns more nearly to its initial thickness immediately after test as the amount of synthetic in the blend increases. It should be recalled, however, that the all-synthetic serges which exhibit maximum thickness recovery are initially half as thick as the fabrics rich in wool (70% wool or more), so that this advantage in form stability under pressure is of little consequence. It is true, however, that some advantage in thickness recovery may be gained from the use of some synthetic in a blend in that the serges containing 30% of synthetic fiber in this series were nearly equal in

TABLE VI. · RESULTS OF THICKNESS-PRESSURE MEASUREMENTS OF BLENDED SERGES

Sample No.	Nominal fiber composition: Wool (%)	Other (%)	a* (mils)	b value*: Loading (lbs./in.)	b value*: Recovery (lbs./in.)	Thickness recovery† (%)
42	100	—	37	2.64×10^{-3}	1.97×10^{-3}	81
8	85	15 Dynel	41	2.61	1.99	83
12	70	30 Dynel	42	2.80	2.20	86
14	50	50 Dynel	40	2.54	1.91	85
15	0	100 Dynel	38	0.44	0.34	94
51	100	—	36	2.21	1.69	84
53	85	15 Acrilan	36	2.56	1.96	83
54	70	30 Acrilan	32	2.28	1.75	84
55	50	50 Acrilan	30	1.54	1.09	82
52	0	100 Acrilan	28	0.50	0.34	88
17	100	—	37	2.91	2.07	77
23	85	15 Orlon	35	2.24	1.71	82
26	70	30 Orlon	35	2.25	1.62	80
28	50	50 Orlon	32	1.94	1.46	83
20	0	100 Orlon	27	0.48	0.34	91

* a and b are constants in the equation $t=a+b/(p+.05)$, in which t and p are thickness and pressure, respectively. a is defined as the thickness at 2.0 lbs./in.^{2} in the present case.

† After one cycle of loading to 0.1 lb./in.^{2} and recovery to 0.002 lb./in.^{2}

thickness to the all-wool controls and exhibited equal or better thickness recovery. The use of some fraction of coarse fibers is again shown to be advantageous with respect to the thickness recovery behavior. This is exemplified by the fabrics containing a substantial amount of Dynel, which exhibit more complete recovery than the corresponding fabrics made with the other (3 den.) synthetics.

Shrinkage in Laundering

Since most Army fabrics are designed to be used and maintained in the field, measurements were made of the dimensional stability of the serges in typical field laundering. Samples were relaxed by immersion for several hours in warm water containing a little wetting agent and tumble-drying. The shrinkage in three launderings using the Army 19-min. washing cycle and Igepon T as detergent, based on the relaxed dimensions, is given in Table VII.

The results indicate that felting shrinkage decreases directly in proportion to the decrease of wool content. This result is in agreement with the data of Whewell [17] and of a number of studies in these laboratories [3] in which it has been shown that nonswellable fibers act as true diluents for wool with respect to feltability.

TABLE VII. FELTING SHRINKAGE IN LAUNDERING OF BLENDED SERGES

Sample No.	Nominal fiber composition Wool (%)	Other (%)	Area shrinkage in three launderings (%)
42	100	—	5.7
8	85	15 Dynel	5.4
12	70	30 Dynel	4.3
14	50	50 Dynel	1.2
15	0	100 Dynel	−0.3
51	100	—	5.4
53	85	15 Acrilan	4.3
54	70	30 Acrilan	4.6
55	50	50 Acrilan	1.2
52	0	100 Acrilan	0.3
17	100	—	5.1
23	85	15 Orlon	4.6
26	70	30 Orlon	3.4
28	50	50 Orlon	2.7
20	0	100 Orlon	1.2

Discussion of Results on Blended Serges

The data obtained from measurements of a series of serges have been presented in Tables I–VII. One over-all effect to be noted is that generally many of the properties evaluated do not change very greatly when up to one-third of the wool is replaced by synthetic; the large-scale changes come about in going from a 50/50 blend to an all-synthetic fabric. The implication in terms of these particular tests is that as much as 30% of these synthetics may be used without substantial alteration of many of the fabric properties.

The results of measurements of thickness, thermal resistance, surface hairiness, and resistance to wetting are believed to be related. Increasing the synthetic content in these fabrics tends to result in a thinner fabric and hence one of lower thermal resistance. The use of higher denier fibers in blending, as in the Dynel series, appears to offer advantages in yielding thicker, warmer, and fuzzier blends which exhibit some degree of resistance to surface wetting by water.

In evaluating the results of such a series of measurements, it becomes clear that one of the intuitive bases on which the analysis of the results tends to be made does not hold—that is, to study the effect on the fabric of the addition of some percentage of an acrylic synthetic to wool, the assumption may be made that the fabrics being compared are identical except for the nature of the fiber and the fiber compositions. These results clearly show that the latter may strongly influence the structure of the fabric that results or that it is possible to make. Thus, such "normal" processing as fulling may become difficult or impossible with high concentrations of synthetics in a blend, and the resulting fabric character will be markedly affected as a consequence of the fulling behavior. In fact, with the present fabrics, this factor may be used to explain most of the observed results.

The Role of Fiber Randomness in Yarns

The degree of randomness or geometrical order of the fibers in the yarn may be a convenient means for visualizing the effects in question. At one extreme, wool fibers exhibit three-dimensional crimp and the fibers encompass a wide range of diameters and length. In a wool yarn, the fibers and fiber segments are therefore randomly distributed compared to some synthetics, and the conformance of each fiber to the yarn geometry is relatively low. Fulling increases the randomness even further, the fibers and fiber segments migrating out from the yarn surface. As a

TABLE VIII. THE EFFECT OF NAPPING ON THE PROPERTIES OF FABRICS

Sample No.	Nominal fiber composition: Wool (%)	Nominal fiber composition: Other (%)	Thickness: At 0.002 lb./in.² (mils)	Thickness: At 1.0 lb./in.² (mils)	Intrinsic thermal resistance: At 0.002 lb./in.² (°C sec. m.²/cal.)	Intrinsic thermal resistance: At 1.0 lb./in.² (°C sec. m.²/cal.)	Bulk density at 0.002 lb./in.² (g./cm.³)	Mean bending length (cm.)	Surface hairiness: Thickness recovery (%)	Surface hairiness: Time to cool 7.5°C (t_1) (sec.)	Surface hairiness: nk/l (cal./°C cm.² sec.)	Drop absorption (0.2 ml.) (sec.)
17	100	0	103	41	.198	.077	0.18	2.2	79	73	7.7×10^{-4}	10,000+
55	50	50 Acrilan	68	32	.142	.060	.19	2.2	82	58	10.9	2,000
55 napped	50	50 Acrilan	107	38	.212	.070	.13	2.4	82	75	7.5	6,000+
28	50	50 Orlon	74	34	.148	.063	.20	2.0	83	69	8.3	1,500
28 napped	50	50 Orlon	112	40	.220	.076	.11	2.3	82	78	7.0	3,000

result, the wool fabric tends to be lofty and hairy, with many fiber arches in the yarn and with many fiber ends protruding from the yarn. An additional factor is that the cross section of the wool fibers commonly employed may correspond to 5 den. or more, which results in a stiffer architecture for the yarn assembly. The greater wool-like character of some of the present Dynel blends as a consequence of the presence of some coarser fiber has already been suggested.

At the other extreme, the synthetic fibers are relatively uniform in length and cross section and tend to conform to the yarn pattern more closely. Despite some advantage in terms of higher modulus, the synthetics commonly are employed in 3-den. sizes so that this advantage is minimized, except for situations in which moisture plays a part, where the synthetics maintain their wet mechanical properties at a high level. Fulling is inoperative so that the original orderly state of the fibers is undisturbed.

It is not intended to suggest that fulling is the only means for creating randomness of the fibers in the yarns; napping may be considered as another means for accomplishing this. Since the blended serges containing 50% Orlon or Acrilan were appreciably thinner and less wool-like than the fabrics of greater wool content, it was considered of interest to demonstrate that napping could be useful in producing a cloth more nearly resembling the all-wool serge in behavior. Specimens of the 50/50 blends were napped in the laboratory with a hand-card to produce a fabric of comparable thickness to the all-wool controls. The results of a limited number of measurements on the same specimens before and after napping are given in Table VIII. The significant effect of napping on the fabric properties measured can readily be seen. The results suggest that fiber randomness with the resulting effects on thickness, fuzziness, and related fabric characteristics may be increased by napping, and that blends rich in synthetic may be made to approach an all-wool serge in some of these characteristics. The experiments on napped fabrics indicate that even the rate of water absorption is influenced by the nature of the fabric surface.

It is tempting to account at least in part for the drop absorption and wicking results in Table IV in this way, the values decreasing in the same sense as the surface hairiness as the wool content decreases. Furthermore, if one considers the wicking in the yarn as a capillary process, those yarns in which the fibers were aligned in an orderly way would be expected to wick more rapidly than would be anticipated in the case of yarns with the fibers arranged in a less orderly fashion in the yarn; in the latter case the capillary size distribution would be such that more discontinuities would occur with fewer total functioning capillaries available for water transport over a given distance. A test of this view was made using a hand-woven fabric which had never been fulled. Specimens of this sample were subjected to a mild felting treatment in a tumble jar containing distilled water and rubber stoppers to provide some mechanical action. The results of longitudinal wicking measurements are given in Table IX both for strips of fabric and for warp yarns removed from the fabric.

The increase in wicking time with increased felting is significant. Microscopic examination of the yarns clearly showed the reduced parallelism of the fibers as a result of the felting. This is thought to be evidence of the effect of fiber randomness on this property. The mechanism by which synthetic fabrics

TABLE IX. EFFECT OF FELTING ON WICKING

Time of tumbling (min.)	Longitudinal wicking: Fabric (sec. per 1-in. rise)	Longitudinal wicking: Yarn (sec. per 1-in. rise)
0	30	100
10	200	260
20	410	440

wick may therefore be less a function of the fiber properties and may involve to a greater degree the geometry of the yarn and the degree of fiber order.

Of the measurements made, the thickness, thermal resistance, hairiness, resistance to wetting or wicking, and thickness recovery may, in whole or in part, be consistent with this view of the role of fiber order. The bending stiffness and crease recovery results are associated in this series with the lower weight of the fabrics with increasing synthetic content. Some of the behavior of the moist fabrics may be accounted for in terms of high wet modulus of the synthetic fibers.

For the purpose of clarifying the problems involved in proper fabric design for the purpose of evaluating blends, it may be desirable to consider ways of increasing the randomness of the fibers, especially in blends containing large amounts of synthetics. Some methods for accomplishing this are as follows: (*1*) the use of mixtures of varying denier and staple length in blending (coarser fibers and shorter staple are indicated); (*2*) the use of crimped fiber; (*3*) napping; (*4*) shrinking of the synthetics by means of heat or swelling agents; (*5*) the use of fulling assistants to promote felting; (*6*) systems of spinning which order the fibers in the yarn to the least extent—*e.g.*, woolen as opposed to worsted spinning.

It is intended to apply several of these principles in fabrication of blends in order to assess the validity of this viewpoint. It would seem possible to manufacture fabrics from blends containing substantial amounts of synthetic which are more nearly similar in character to wool fabrics than those in the series described here.

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Mechanical Conditioning of Textile Fibers*

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Abstract

Mechanical conditioning denotes the alterations which remain temporarily or permanently in textile fibers after they have been deformed. These alterations are the result of changes in the structure of textile fibers. The altered tensile properties, including tensile recovery behavior, of mechanically conditioned fibers were investigated.

Cotton, Fortisan, Ethocel, acetate, silk, viscose, Dacron polyester fiber, Orlon acrylic fiber, Vicara, Vinyon NORU, casein, Nylon Type 300, Saran, human hair, and wool were tested either as single fibers, as multifilaments, or as staple yarns. Mechanical conditioning was performed mostly by repeated extensions (cycling) to 80% of the extensibility. The response of fibers to this procedure varies widely. If a fiber is susceptible to mechanical conditioning due to its visco-elastic behavior, its morphology (length, cross section) and stress-strain properties are altered considerably.[1] The new extensibility and the work of rupture decrease, and the elastic recovery increases. The initial modulus and the breaking tenacity can remain unchanged; they can increase or they can decrease. The yield point can become more or less pronounced, or it can increase or decrease; even new yield points can appear after mechanical conditioning.

In connection with mechanical conditioning, the following topics were investigated: (*1*) alterations occurring spontaneously or produced by heat and swelling after mechanical conditioning of cellulose acetate; (*2*) structural changes of cellulose fibers due to stretching (stress hardening and fatigue); (*3*) cold-drawing of a Dacron monofilament; and (*4*) behavior of a cotton thread after repeated extensions to different strain levels.

Introduction

It is a peculiarity of visco-elastic materials that their properties are influenced by their previous history. If they have been deformed, the magnitude and duration of that deformation and the relaxation following will be reflected in their subsequent behavior.

The tensile properties of textile fibers are characterized by the stress-strain relationship and tensile recovery. These are by no means always the same for a given fiber, even under identical conditions of environment and time factors. If the elastic limit has been exceeded in extending a fiber, its stress-strain relationship and tensile recovery will be different in a subsequent extension. The deformation affects the fiber structure, and this is manifested by altered tensile properties after the tension is released. To some extent, the modification is temporary, since fibers may partially recover after a while, and only some of the properties remain permanently changed. Various textile materials differ widely in their response to deformations, some being more easily affected than others. This alteration is known as "mechanical conditioning."

Elastic fibers remain almost unchanged after a deformation. On the other hand, an extension markedly affects less elastic fibers having high permanent set values. Figure 1 demonstrates the changes produced by mechanical conditioning in the stress-strain curves * of six fibers with different extensibilities and recovery behavior—multifilaments of Fortisan, Saran, regular viscose, Nylon Type 300, acetate, and a worsted wool yarn. Their elongations at break before mechanical conditioning are 7.1%, 15.3%, 15.7%, 21.4%, 24.3%, and 33.2%, respectively. The samples were extended to 80% of their elongation at break in 50 cycles and tested again after a relaxation time of 1 hr. There is not much difference between the stress-strain curves of Saran before and after mechanical conditioning since Saran is highly elastic.

* A part of this study was the subject of a paper given at the Spring Meeting of The Fiber Society at Clemson, S. C., April 17, 1952. The article has also been published as Textile Series Report No. 82 by the Department of the Army, Office of the Quartermaster General, and is available through the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

* In Figures 1 and 2 elongation and uncorrected tenacity values after mechanical conditioning are correlated to the new fiber length and new fiber fineness corresponding to the demonstration of curve *IV* in Figure 5A.

The breaking point remains practically unchanged, but a lower initial modulus appears after repeated extensions. The alteration of Fortisan, nylon, and wool * by cycling is only moderate. They represent fibers with considerable elastic recovery and relatively low permanent set. However, the cycling markedly changed the stress-strain curves of the less elastic fibers, viscose and acetate, reflecting their substantially decreased extensibility, as shown in Figure 2. The relative values of permanent set at the breaking point † are 13% for Saran, 28% for Fortisan and nylon, 41% for wool, 61% for viscose, and 70% for acetate. These data demonstrate that the alteration of the original stress-strain curve increases with the permanent set of the fibers. The new stress-strain relationship with diminished extensibility indicates also the reduction of permanent set values during the stretching procedure.

Each fiber is affected to a greater or lesser extent if deformed to different degrees. The stress or strain to which a fiber has been stressed or extended is known as "conditioning level." It can be expressed either by actual values (*e.g.*, g. load, g/gx. tenacity, % elongation, g.-cm./gx. work) or by relative values (as the percentage of ultimate stress, strain, and work of rupture). The degree of alteration after an extension depends partly on the magnitude of unrecovered elongation at the conditioning level. This illustrates the usefulness of knowing the recoverable and unrecoverable portions of the total elongation for any stress and strain value. These are not indicated by the conventional stress-strain curves, but are readily obtainable by an analysis of the stress-strain relationship which divides total elongation into three components: immediate elastic recovery, delayed recovery, and permanent set [33]. It is obvious that the immediately recoverable portion does not contribute at all to the alteration of a fiber after the tension has been released. The influence of delayed elastic recovery on fiber properties is only temporary. The permanent set, however, reflects irreversible structural alterations manifested in new and permanent stress-strain properties. Therefore, the elongation components, if known quantitatively, indicate to what extent a fiber will be affected by extending to different conditioning levels. The two quadratic graphs of Figure 3 demonstrate the recovery behavior of an acetate multifilament from the beginning of the stretching procedure up to rupture. The relative values of the three elongation components shown in the graphs were obtained by a previously described cycling technique [33] using a single extension and 5-min. relaxation time to separate delayed recovery from permanent set. The elastic limit (yield point) appears at 16% of the elongation and at 67% of the tenacity at break (light dashed line). Below the yield point an immediate elastic recovery of 74% and, consequently, a delayed recovery of 26%, without any permanent set, are demonstrated. It can be expected, therefore, that a small and almost unde-

* The initial flat portion on the curve of mechanically conditioned wool represents the recovered crimp of the single fibers in the yarn structure, as described in a previous publication [34].

† Obtained in a single extension; listed in Table II.

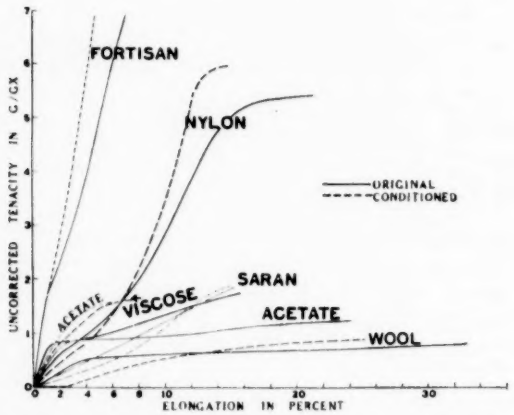


FIG. 1. *Stress-strain curves of 6 fibers before and after mechanical conditioning.*

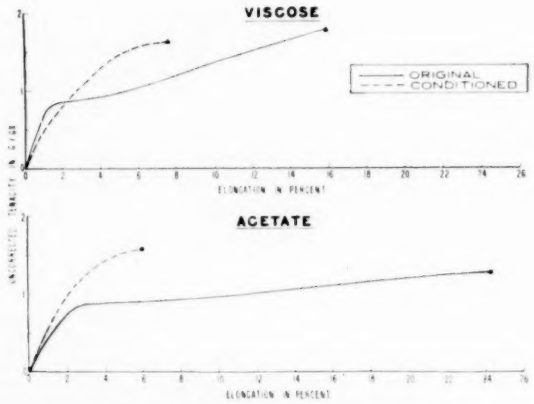


FIG. 2. *Stress-strain curves of viscose and acetate before and after mechanical conditioning.*

tectable alteration of the acetate multifilament will occur after an extension to a point below the yield point when tested immediately after releasing the tension. However, if tested after a relaxation time of 5 min., no alteration at all will appear. On the other hand, if this fiber is extended to a higher conditioning level—say, to 40% of the extensibility, corresponding to 75% of the tenacity at break (medium dashed line)—a pronounced change can be expected immediately after the extension, since only 33% of this elongation recovers immediately. A part of the elongation, 28%, remains unrecoverable even after the 5-min. relaxation time, reflecting permanent structural changes. The alteration of the fiber will be more pronounced, of course, if extended to a point closer to the breaking point—say, to 80% of the elongation or to 90% of the tenacity at break (heavy dashed lines)—since permanent set is the predominant component (64%) of the total elongation at this level. The two quadratic graphs also reveal that it will not make much difference whether the fiber is extended to 80% of the elongation at break (as in the tests shown in Figures 1 and 2) or to a point closer to rupture, since permanent set remains almost unchanged in this region (from 64% to 70%). In contrast to this, notable differences can be expected between fibers extended to 80% of the tenacity at break (dotted line) and to a point closer to rupture due to the marked differences in permanent set (from 42% to 70%) at these levels.

Although it is possible to estimate the behavior of fibers after an extension if their elongation components are known quantitatively, it is not possible to predict exactly their new stress-strain and recovery behavior. The effect of a tensile deformation does not consist merely in the elimination of permanent set and a decrease in the extensibility of the fiber; it can also affect other tensile properties. This is demonstrated schematically in Figure 4. Curve *I* represents the load-elongation relationship of a fiber having an extensibility of 20% and a breaking load of 160 g. When the fiber is elongated to 75% of its elongation at break, to the conditioning level *M* on the schematic curve (corresponding to 15% actual elongation or to 140 g. load), the response of the fiber can be different. Three types of conditioned curves can be obtained (curves *II*, *III*, and *IV*) reflecting three different alterations of the fiber structure during the deformation process. They demonstrate how

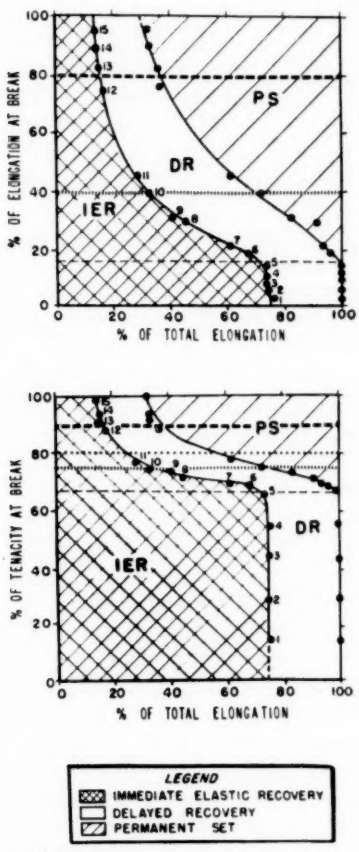


FIG. 3. *Elongation components of acetate multifilament at various strain and stress levels.*

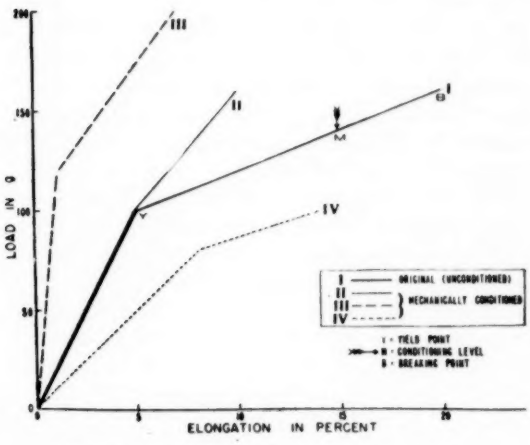


FIG. 4. *Schematic load-elongation curves.*

differently fibers can respond when extended to the same level. If the permanent set is eliminated without affecting the original extensibility of the fiber (20%), new extensibilities of 14%, 10%, and 7% remain after mechanical conditioning. They indicate three different amounts of permanent set, 6%, 10%, and 13%, eliminated by conditioning. On all three curves marked decreases in extensibility and work necessary for rupture become apparent. In addition, curve *II* is characterized by unchanged tensile properties in the initial part of the curve up to the yield point *Y* (apparent from unaltered yield load, yield elongation, and initial modulus) and by the unchanged breaking load of 160 g. Curve *III* shows not only a higher initial modulus than originally, but a higher yield and breaking load (200 g.), while the yield elongation and the total extensibility decrease. Thus, there is not much similarity remaining between curves *III* and *I*. This type of response reveals stress hardening. Stiffening, increased breaking load, and diminished extensibility are not unusual in textile fibers after stretching or drawing. They are due to structural changes of the fiber known as "orientation." Curve *IV* is also rather different from the original. It shows decreased initial modulus, yield and breaking load, extensibility, and work necessary for rupture. These characteristics indicate a weakening of the fiber as a result of "fatigue" due probably to slippage, crystal lattice distortion, or to formation of cracks; it is readily observable in "overstretched" fibers.

Any structural change of solids is connected with altered physical properties, especially mechanical properties. Perfectly elastic materials and solid bodies representing undercooled liquids with high "viscous flow" cannot be mechanically conditioned. In perfectly elastic materials, as in crystals, the structural changes introduced by deformation disappear as soon as the deforming force is released. In ordinary liquids, the deformation proceeds at a constant rate proportional to the force without permanent structural changes. Textile fibers consist of crystalline and amorphous materials. They have visco-elastic properties and behave partly as crystalline solid materials and partly as undercooled liquids. Under certain circumstances they can be mechanically conditioned to very different degrees according to their inherent properties. The alterations of their structure are then reflected not only in changed tensile and transverse properties (in bending, torsion, and shear), but also in changed morphology (length, thickness) and physical and chemical properties—density, optical behavior (birefringence and luster [28]), swelling and shrinkage, moisture absorption, dyeability [25, 27], chemical reactivity [29], etc.

The drawing of synthetic fibers is a typical case of mechanical conditioning, and it consists of stretching plastic fibers under controlled conditions to eliminate such undesirable properties as excessive extensibility, high permanent set, and low initial modulus of elasticity. This is generally accompanied by the acquisition of some desirable properties—high elastic recovery and tenacity, decreased swelling, and luster. It can also be connected with the sacrifice of advantageous properties such as transverse strength or dyeability [25, 27]. The deformation of filaments in the wet or dry fiber spinning process is similar to the drawing process. This is generally not considered mechanical conditioning, but is designated as stretching, and it is carried out on an unfinished fiber. Essentially, however, there is no difference between the stretch-spinning of a viscose filament with its hardened skin and semiliquid core and the cold or hot drawing process of synthetic fibers (nylon, Dacron, Vinyon, polyethylene, Saran) if the stretching procedure is considered.

The properties of natural, man-made, and synthetic fibers are altered by tensile deformations during various steps of yarn spinning, fabric weaving, and finishing processes. These alterations are at least partly unintentional and are generally less pronounced than the above-discussed deliberately produced deformations in the stretching or drawing processes. Unintentional mechanical conditioning of textile fibers also occurs during use, because yarns and fabrics are subjected in service to frequent deformations which are invariably connected with a progressive alteration of the original fiber properties. Even low deformations, if frequently repeated, can markedly alter the behavior of textiles. The effect of high or often-repeated deformations which are detrimental in service is known as "fatigue."

Mechanical conditioning of fibers covers a large field. This study, however, is restricted to intentional tensile deformations of fibers.

Mechanical conditioning of fibers can be carried out either by a constant or an alternating (cycling) stress or strain. If constant stress is applied, either for a long period of time or by cyling, the fiber length increases progressively and consequently the cross

section and grex decrease. This procedure generally causes rupture at a stress markedly lower than in a single loading step due to plastic flow (increasing permanent set) and to high stress concentration. On the other hand, if the fiber is extended constantly or in successive cycles to the same strain level, the tension decreases during the extension and a "load decay" or "stress relaxation" occurs. This prevents early rupture except when marked weakening takes place as a result of excessive plastic flow, slippage, or fatigue. Mechanical conditioning due to the application of stress is therefore more severe than that by strain equivalent to the stress.

Historical Background and Definition of Mechanical Conditioning

Weber [35] was the first to investigate a mechanically conditioned fiber. In 1835 he described the decreased extensibility and the enhanced elasticity of stretched silk filaments and the elimination of unrecoverable elongation (permanent set) in consecutive loading steps. The term "mechanical conditioning," now widely accepted, was first used in textile literature in 1941 by Leaderman [22]. He defined mechanical conditioning as a tensile deformation which eliminates subsequent "secondary creep" (permanent set). Decrease in extensibility and elimination of permanent set are striking alterations of fibers due to mechanical conditioning. They are, as stated above, not the only alterations, although it seems that all other changes are associated with this process. In a broader sense, "mechanical conditioning" should connote, therefore, any alterations of fiber properties by mechanical procedures where they remain temporarily or permanently after the deforming force is released. Mostly, however, only tensile deformations (by forces acting parallel to the fiber axis) are understood to be mechanical conditioning. The term "mechanical conditioning" indicates the transformation of various samples of a textile material having different extensibilities and recoveries (due to differences in their straining history) into similar and more comparable forms by a mechanical process. This procedure reduces their extensibility and enhances their recovery, and it is in some way analogous to the well-known conditioning of textiles in a standardized atmosphere to bring them into a comparable state.

Although no systematic study has been published on mechanical conditioning of textile fibers, numerous investigators have discussed in one way or another the altered behavior of fibers after tensile deformations. Papers have been published by Abbott [1], Boehringer [3], Brenschede [4], Burte [5], Busse and coworkers [6], de Vries [7], Eyring and coworkers [8, 9], Hamburger [10], Jaeger [15], Kaswell [19], Kochanski [21], Leaderman [22, 23], Meredith and Peirce [24], Munden and Palmer [25], O'Shaughnessy [26], Pinte and coworkers [27, 28, 29], Souther [32], Wegener [36, 37], Wenderoth [38], Zart [39], etc. It is interesting to note in this connection that Ivarsson [14] thoroughly investigated the mechanical conditioning of paper. He was able to interpret the tensile behavior of this visco-elastic material before mechanical conditioning in terms of Eyring's theory [8] using a three-element model consisting of two ideal springs and a dashpot. After the paper was mechanically conditioned, however, an exact representation of the tensile behavior by the model could no longer be obtained.

Demonstration of the Stress-Strain Relationship

Some difficulties are involved in demonstrating the effect of mechanical conditioning by the stress-strain relationship. Of the numerous possible methods, that one should be accepted which best reproduces the actual conditions without undue complexity and also permits a fair comparison of tensile properties before and after conditioning, even when the conditioning history is unknown. Of course, in performing mechanical conditioning tests the stretching procedure is known. It frequently occurs, however, that the tensile properties of unstretched, partly stretched, or fully stretched fibers have to be evaluated and compared without the necessary information on the stretching or drawing process itself.

A widely accepted method of demonstrating the tensile properties of textile fibers consists of plotting uncorrected tenacities *—*e.g.*, load in grams per initial fineness (grex)—against elongation—length increase expressed as percent of the original length. Curve *1* in Figure 5A shows the stress-strain relationship of an acetate multifilament in this way, with the breaking point at 1.25 g./gx. tenacity and at 24.3% elongation. After mechanical conditioning (to 80% of the extensibility in 50 cycles and 1 hr. relaxation) the fineness of the acetate multifilament decreases from 111 to 95 grex and the fiber length increases by

* The initial fiber fineness is here considered to remain unchanged during the stretching procedure, which actually is not the case.

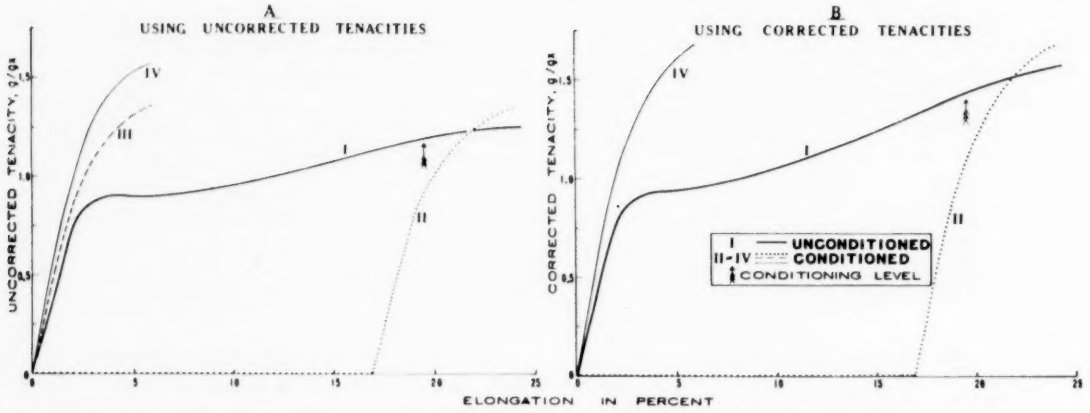


FIG. 5. *Stress-strain relationship of acetate multifilament, using different methods of presentation.*

16.9%. If the stress-strain relationship of the conditioned acetate is to be demonstrated, two questions arise: which fineness and which length should it be based upon, the original or the new?

There are many ways of presentation, three of which are shown in Figure 5A using uncorrected tenacities, as for curve *I*. In curve *II* tenacities are based on the original fineness (111 grex), and the elongation is also correlated to the original fiber length before conditioning. An initial flat portion appears on this stress-strain curve, representing the length increase of the fiber by permanent set. The tension starts at 16.9% elongation after the slack has been removed from the mechanically conditioned fiber. A slightly increased tenacity (from 1.25 to 1.35 g./gx.) and practically unchanged over-all extensibility (23.9% compared to 24.3%) appear at the breaking point. This demonstration can be recommended for tests performed immediately after mechanical conditioning without removing the sample from the tester.

In curve *III*, tenacities based on the fineness before conditioning (111 grex) are plotted against elongation values correlated to the new increased fiber length. No initial flat portion and therefore a considerably lower extensibility (6.0%) are shown. This curve corresponds, but is not identical, to the curved-end portion of the foregoing demonstration (curve *II*).

Finally, in curve *IV* tenacities are based on the new fineness (95 grex), and the elongations are also correlated to the new increased fiber length after conditioning. Here a markedly higher tenacity than originally (1.58 compared to 1.35 g./gx.) appears at the same elongation (6.0%) as in curve *III*. For this presentation it is not necessary to know the fineness before conditioning and the length increase during the conditioning procedure. The conditioned sample is considered here as an entirely new fiber, and its properties are evaluated in the same manner as those of any other unconditioned fiber. This demonstration is practicable, therefore, even when data necessary for the previous two demonstrations are unavailable. Its use, however, seems scarcely justified for describing tests on mechanical conditioning.

It is convenient and simple to correlate stress values to an unchanged initial fineness, and this method may have some advantages for textile fibers. Nevertheless, the tenacity values appear distorted more or less according to the extensibility, since fineness does not remain constant but changes progressively during stretching. Uncorrected tenacities therefore have the disadvantage of being in some way unrealistic. This deficiency can be eliminated by taking the diminishing grex into account and using corrected tenacities in which stress values are correlated to the decreased grex. The decreased grex can be calculated approximately from the initial fineness and the elongation, assuming that a uniform stretching takes place over the entire fiber length. In the three curves of Figure 5B, the stress-strain relationship of the acetate multifilament is replotted before (curve *I*) and after mechanical conditioning (curves *II* and *IV*) using corrected tenacities. Similar to the demonstrations in Figure 5A, the elonga-

tion values are correlated to the original fiber length and fineness (111 grex) before conditioning in curves *I* and *II*, and to the increased new length and decreased grex (95) in curve *IV*. Corrected tenacities are always higher than uncorrected values. In this case the mechanical conditioning also slightly increased the corrected tenacity (from 1.56 to 1.67 g./gx.). The rate of this increase is practically identical, however, to that for uncorrected values. Contrary to the demonstration in Figure 5A, no difference appears in the corrected tenacities of curves *II* and *IV* (even though curve *II* was based on 111 grex and curve *IV* on 95 grex) since decrease of fineness during testing was taken into account in both cases. Presentation by corrected tenacities would probably be more advantageous than by uncorrected tenacities, but it was not adopted in this study because it is not used widely enough in testing textile fibers.

It is obvious that these five methods of presenting mechanically conditioned fibers do not influence only the ultimate values since yield point, initial modulus of elasticity, and work necessary for rupture are also affected. Therefore, data on tensile properties of mechanically conditioned fibers must always indicate which method was used for the evaluation. Unless otherwise stated, the stress-strain curves of conditioned fibers presented in this study will show uncorrected tenacities based on the original fineness before conditioning plotted against elongations, expressed as percentages of the new fiber length after conditioning. This method, which is demonstrated in curve *III* of Figure 5A, permits a satisfactory comparison of tensile properties before and after conditioning, but it is by no means free from disadvantages. In some instances, therefore, this presentation was abandoned and replaced by others which were thought to be more suitable for the particular case involved (*e.g.*, in Figures 1, 2, 13, 15, 21B, and 23).

Experimental Procedure

All the fibers were mechanically conditioned by extending them to a given strain level; in most cases they were repeatedly extended (cycled) and in a few cases they were held extended. The extension of fibers was carried out in various ways. The conditioning level and procedure were kept constant in testing different fibers of a series. The conditioning level was varied in investigating the response of the same fibers (viscose multifilament, undrawn Dacron monofilament, 56/3 cotton thread) to different strains. Any changes made in the conditioning procedure to meet particular requirements will be indicated in the discussion.

All tests were performed at 70°F (21.1°C) and 65% relative humidity using the Instron tensile tester, model TT-B.

Mechanical Conditioning of 16 Textile Fibers

The effect of mechanical conditioning was investigated first on 16 samples, including single fibers, multifilaments, and staple yarns. This series demonstrates the alteration that occurs in textile fibers of nearly every type after repeated strains to a constant and relatively high elongation level. This elongation level was equivalent for all the fibers tested with the exception of Ethocel, and it necessarily corresponded to different actual strain values.

The samples were extended in the Instron tensile tester 50 times to 80% of their elongation at break * using an 8-in. (20.3 cm.) gage length and a jaw separation corresponding to 62.5% elongation per minute. Then they were relaxed without tension for 1 hr. and finally tested for their stress-strain relationship using a 5-in. (12.7 cm.) gage length and a jaw separation of 100% elongation per minute. The length increase attained during the stretching procedure was measured immediately after cycling and also after the relaxation period. Average stress-strain curves, each obtained on at least 10 specimens before and after mechanical conditioning, are demonstrated in Figures 6 and 7. Table I shows the corresponding numerical data in addition to some other values (fiber length and fineness, initial modulus, corrected tenacity, etc.) important to the evaluation of mechanically conditioned fibers.

The most evident alteration of fibers after extension is their increased length. The length increase of the fibers tested was between 1.3% and 25.1% immediately after cycling. This is quite considerable in view of the fact that they originally had extensibilities between 5.5% and 44.4%. The new fiber length by no means remained constant; it decreased (at a diminishing rate with time) as a result of delayed recovery or primary creep. Thus, all conditioned fibers shrank during the relaxation period of 1 hr., but not one regained entirely its original

* Mechanical conditioning of Ethocel was not possible at 80% due to its unevenness (see column 3, Table I). It was extended only to 70% of the elongation at break.

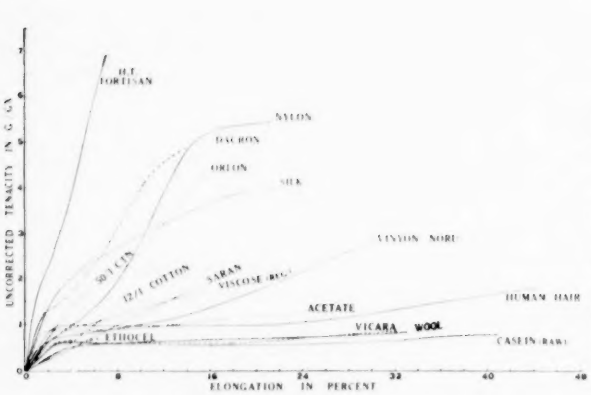


FIG. 6. *Stress-strain curves of 16 fibers before mechanical conditioning.*

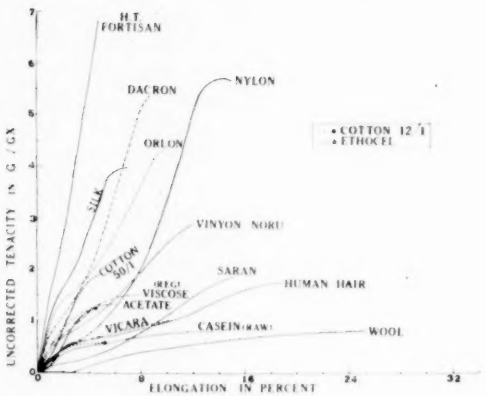


FIG. 7. *Stress-strain curves of 16 mechanically conditioned textile fibers.*

length. The shrinkage was relatively small (approximately 1% for most of the fibers tested), indicating partly reversible structural changes. Only the protein fibers with high elastic recovery shrank appreciably more: Vicara (2.5%), human hair (2.6%), and wool (6.3%). The marked difference in the shrinkage of the two keratin fibers (hair single fiber and wool yarn) was interpreted in a previous study [34] as rebuilt crimp in the wool yarn during relaxation. After 1 hr. relaxation, the length of conditioned fibers remained fairly constant in most cases. Thus, the length increase after this relaxation period (correlated to the original length) was considered as permanent set attained during the cycling procedure, and it was responsible for the new diminished grex. The length increase for the majority of the fibers tested was between 5% and 20% of the original length. If this value was large in comparison to the original extensibility, a marked alteration of tensile properties took place.

The new extensibility of the fibers tested was less after conditioning than originally if correlated to the new fiber length (column 13, Table I). The decrease was slight for the elastic fibers Saran, Ethocel, 50/1 cotton, wool, nylon, and Fortisan; more pronounced for Orlon, 12/1 cotton, viscose, and Dacron; and considerable for human hair, Vinyon NORU, casein, silk, Vicara, and acetate. The over-all extensibility of the conditioned fibers (column 16, Table I),* however, remained in many cases practically unchanged, 96%–101% of the original. The over-all extensibility of silk and Vicara was slightly reduced to 88% and 91% of the original, while that of Ethocel, Saran, Orlon, and of the staple yarns (cotton and wool) increased to 106%–118% of their original extensibility.

It is of some importance to know whether a fiber has been weakened or strengthened by the stretching procedure. In order to answer this question, it is advisable to compare breaking loads directly instead of tenacities to avoid any distortion of actual stress values. The breaking loads of 11 of the 16 fibers tested after mechanical conditioning were between 97% and 105% of the original values. These fibers can be considered as being unaffected by the cycling procedure in view of the unevenness of the samples and of possible errors in testing. Only viscose, 12/1 cotton, and Ethocel showed a decrease in breaking load (86%–92% of the original) after cycling, indicating some fatigue; while the breaking load of acetate and Vicara increased slightly (108%–118% of the original), indicating a slight stress hardening.

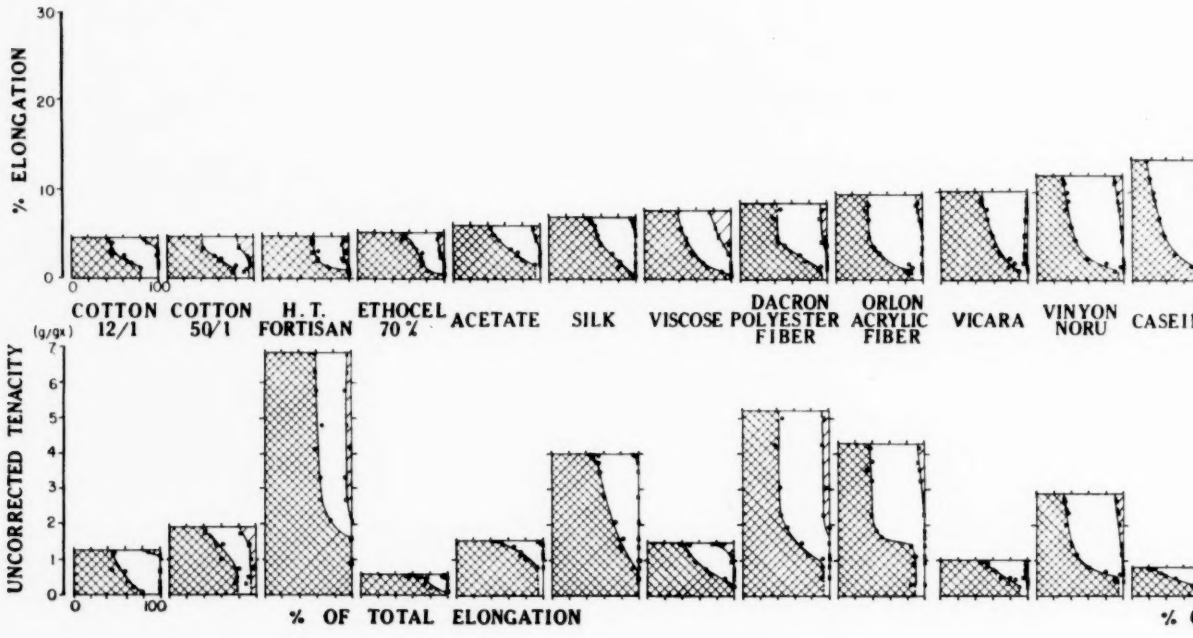
In most cases, the total work absorption of fibers decreased considerably after mechanical conditioning, since the extensibility was reduced and the breaking load was only slightly affected. It must be noted that the work necessary to elongate mechanically conditioned fibers to a strain level not markedly exceeding the conditioning level remains fairly constant in consecutive extensions. This is in contrast to the behavior of almost all fibers before mechanical conditioning, since the work of absorption diminishes

* Over-all extensibility is the sum of the length increase attained in cycling (listed in column 10) and the new extensibility (listed in column 15), both based on original length.

TABLE I. STRESS-STRAIN DATA OF

	1	2	3	4	5	6	7	8	
	BEFORE MECHANICAL CONDITIONING								
	Orig. fineness (grex)	Elong. at break[1,2] (%)	Coeff. of var. (%)	Load at break (g.)	Uncorrected tenacity[1,2] (g./gx.)	Coeff. of var. (%)	Corrected tenacity at break (g./gx.)	Init. modulus[1,2] (g./gx.)	In
1. Cotton, staple yarn 12/1	585	8.2	4.9	833	1.42	6.3	1.55	13	
2. Cotton, staple yarn 50/1	118	5.7	7.0	223	1.88	6.4	1.98	35	
3. HT Fortisan, multifilament	100	7.1	5.6	696	6.96	7.2	7.45	196	
4. Ethocel, multifilament	642	5.5	25.4	408	0.63	3.2	0.66	23	
5. Acetate, multifilament	111	24.3	5.1	139	1.25	2.3	1.56	37	
6. Silk, multifilament	117	21.8	5.4	471	4.02	2.5	4.89	72	
7. Regular viscose, multifilament	111	15.7	8.9	195	1.75	5.7	2.02	69	
8. Dacron polyester fiber, multifilament	111	18.1	7.7	586	5.28	1.5	6.25	92	
9. Orlon acrylic fiber, multifilament	111	15.9	3.1	482	4.34	3.9	5.03	90	
10. Vicara, single fiber	3.33	32.3	4.6	2.87	0.86	6.0	1.14	28	
11. Vinyon NORU, multifilament	111	30.3	3.2	310	2.79	5.4	3.64	41	
12. Casein, multifilament	333	41.0	7.8	259	0.78	4.3	1.10	22	
13. Nylon Type 300, multifilament	111	21.4	9.8	606	5.45	1.3	6.63	33	
14. Saran, multifilament	222	15.3	5.2	419	1.88	4.8	2.18	12	
15. Human hair, single fiber	50.2	44.4	8.2	90.4	1.82	3.7	2.63	45	
16. Wool, staple yarn	315	33.2	17.2	265	0.84	15.5	1.12	15	

[1] Shown in Figures 1 and 2. [2] Shown in Figure 6. [3] Shown in Figure 7. [4] Without permanent length increase listed in column 10. [5] Including permanent



A OF THE 16 FIBERS TESTED

9	10	11	12	13	14	15	16	17	18	19	20	21	22
	Length increase (% of orig. length)			AFTER MECHANICAL CONDITIONING									
					Elongation at break				Uncottected tenacity at break (g./gx.)				
Immed.	After 1 hr. relax.	Shrinkage in 1 hr.	New fineness (grex)	% of new length[1,2]	Coeff. of var. (%)	% of orig. length[1]	% of orig. length[3] (over-all extensibility)	Load at break (g.)	Corrected to the orig. grex[2]	Coeff. of var. (%)	Corrected to the new grex[1]	Corrected tenacity at break (g./gx.)	Init. modulus[3] (g./gx.)
5.6	5.0	0.6	556	4.5	8.7	4.72	9.72	726	1.24	4.9	1.30	1.36	47
2.5	1.9	0.6	116	4.7	10.6	4.79	6.69	225	1.91	4.7	1.94	2.03	54
2.5	1.9	0.6	98	4.8	4.2	4.89	6.79	683	6.83	6.6	6.96	7.25	179
1.3	0.6	0.7	639	5.2	13.5	5.23	5.83	375	0.58	3.4	0.59	0.62	22
17.8	16.9	0.9	95	6.0	9.8	7.00	23.90	150	1.35	1.8	1.58	1.67	46
11.9	11.2	0.7	106	7.0	11.8	7.83	19.03	466	3.98	3.4	4.40	4.71	114
8.1	7.5	0.6	103	7.7	20.8	8.30	15.80	167	1.51	7.7	1.62	1.75	55
9.4	8.8	0.6	102	8.7	5.9	9.46	18.26	596	5.38	1.8	5.83	6.46	80
8.8	7.5	1.3	103	9.7	3.1	10.40	17.90	486	4.83	3.9	4.72	5.17	97
20.0	17.5	2.5	2.84	10.1	16.3	11.88	29.38	3.39	1.02	13.3	1.20	1.32	22
17.5	16.2	1.3	95	11.9	4.9	13.83	30.03	321	2.89	5.8	3.36	3.75	41
25.1	23.8	1.3	269	13.7	11.5	16.91	40.71	273	0.82	3.9	1.02	1.16	20
6.3	5.0	1.3	106	15.0	6.7	15.79	20.79	631	5.67	0.9	5.95	6.82	22
3.1	1.9	1.2	218	15.1	2.7	15.39	17.29	418	1.88	6.4	1.92	2.21	14
23.8	21.2	2.6	41.4	18.9	6.8	22.90	44.10	90	1.79	5.3	2.17	2.58	23
16.9	10.6	6.3	285	25.3	17.5	28.0	38.60	258	0.82	8.7	0.91	1.14	11

manent length increase listed in column 10.

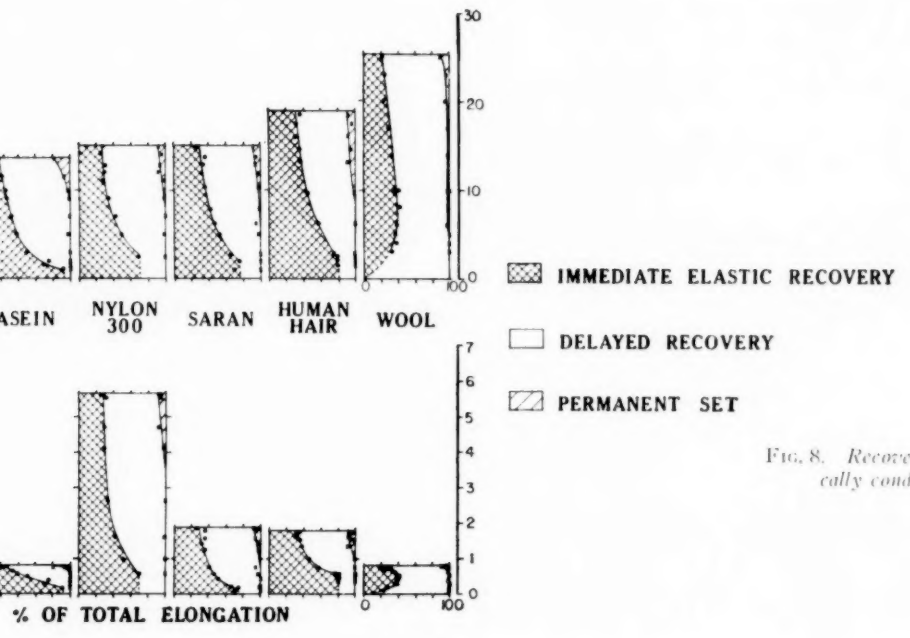


FIG. 8. *Recovery behavior of 16 mechanically conditioned textile fibers.*

after the first elongation if the elastic limit (yield point) has been exceeded in the extension. It is obvious that mechanical conditioning changes the initial modulus of elasticity and also the entire stress-strain relationship of fibers. The wide variety in the shape of the stress-strain curves with more or less pronounced yield points, as demonstrated in Figure 6, almost disappears. After mechanical conditioning, the curves for the most part become more similar to each other with less distinct yield points, as shown in Figure 7.

Due to the elimination of permanent set, mechanically conditioned fibers exhibit high elastic recovery (resilience). As mentioned above, the first observation of mechanical conditioning by Weber [35] was based on this behavior of an extended silk filament. A marked increase in elastic properties after mechanical conditioning was also observed by Leaderman [23], Hamburger [10], Meredith and Peirce [24], and other investigators.

The recovery behavior of the 16 fibers tested after mechanical conditioning is illustrated in Figure 8 by rectangular graphs in which relative values of the three elongation components—immediate elastic recovery, delayed recovery, and permanent set—are plotted against actual strain and stress values.* The fibers are shown without exception as being highly elastic materials, with permanent set appearing only as a small area near rupture. The permanent set would be even smaller if the mechanical conditioning were carried out to a point closer to rupture, and, of course, larger if the conditioning level had been lower than 80% of the elongation at break.

Numerical data of actual and relative values of the elongation components at the breaking point before and after mechanical conditioning are listed in Table II. The increase in elasticity and elimination of permanent set by mechanical conditioning are apparent from the considerably decreased actual and relative values of permanent set in this table. The actual values vary for unconditioned fibers from 0.8% to 25.0% and for conditioned fibers from 0.3% to 3.0%. As for the other elongation components, the actual values of immediate elastic recovery remained practically unchanged (except for Vicara), while the relative values increased only because of the reduced extensibility to which they were correlated. The

* The recovery behavior of these fibers before mechanical conditioning was demonstrated by rectangles in two previous publications (Figure 7B [33] and Figure 5 [34]).

TABLE II. RECOVERY DATA OF THE 16 FIBERS TESTED AT THE BREAKING POINT

	1	2	3	4	5	6	7	8	9	10	11	12
	Before Mechanical Conditioning						*After Mechanical Conditioning*					
	Actual values[1]			Relative values[2]			Actual values[3]			Relative values[4]		
	Recovery			Recovery			Recovery			Recovery		
	Immediate elastic	Delayed	Permanent set	Immediate elastic	Delayed	Permanent set	Immediate elastic	Delayed	Permanent set	Immediate elastic	Delayed	Permanent set
1. Cotton, 12/1	2.1	2.5	3.6	26	30	44	1.9	1.7	0.9	42	38	20
2. Cotton, 50/1	2.5	1.8	1.4	44	32	24	1.9	1.9	0.9	40	40	20
3. HT Fortisan	3.1	2.0	2.0	44	28	28	2.8	1.7	0.3	58	36	6
4. Ethocel	2.8	1.9	0.8	50	36	14	2.7	2.1	0.4	52	40	8
5. Acetate	3.4	3.9	17.0	14	16	70	2.6	2.9	0.5	44	48	8
6. Silk	3.4	4.5	13.9	16	20	64	3.2	3.3	0.5	46	47	7
7. Viscose	3.0	3.1	9.6	19	20	61	3.0	2.8	2.0	38	36	26
8. Dacron polyester fiber	3.3	6.7	8.1	18	37	45	3.6	4.4	0.7	42	50	8
9. Orlon acrylic fiber	3.3	5.9	6.7	21	37	42	3.4	5.5	0.8	36	56	8
10. Vicara	2.3	11.6	18.4	7	36	57	4.8	5.0	0.3	48	49	3
11. Vinyon NORU	3.6	8.5	18.2	12	28	60	3.8	6.9	1.2	32	58	10
12. Casein	4.1	11.9	25.0	10	29	61	2.6	8.4	2.7	18	62	20
13. Nylon Type 300	3.9	11.5	6.0	18	54	28	3.9	9.9	1.2	26	66	8
14. Saran	5.0	8.3	2.0	33	54	13	4.5	9.4	1.2	30	62	8
15. Human hair	6.2	18.6	19.6	14	42	44	6.0	11.2	1.7	32	59	9
16. Wool	5.0	14.6	13.6	15	44	41	5.6	16.7	3.0	22	66	12

[1] In % of original fiber length.
[2] In % of elongation at break (column 2, Table I).
[3] In % of the new fiber length after mechanical conditioning.
[4] In % of elongation at break after mechanical conditioning (column 13, Table I).

actual values of delayed recovery diminished in most cases after conditioning, but not nearly so much as those of permanent set. For a few elastic fibers (50/1 cotton, Ethocel, Saran, and wool) even a slight increase in actual values of delayed recovery was observed. The relative values of delayed recovery increased without exception for the same reason, however, as those of immediate recovery.

It is interesting to compare the responses of the two cotton yarns, 12/1 and 50/1, to repeated extensions as revealed by the numerical data in Tables I and II. The 50/1 yarn with the higher twist * was less extensible (5.7% compared to 8.2%), stronger (1.88 compared to 1.42 g./gx.), and more elastic (relative value of permanent set at the breaking point was 24% compared to 44% for the 12/1 yarn). Accordingly, the length increase of the 50/1 yarn was much less after cycling whether compared immediately or after the relaxation period (see columns 9 and 10, Table I). The effect of mechanically conditioning the two yarns was to make their extensibilities similar when correlated to the new length (4.7% and 4.5%). Their over-all extensibilities (6.69% and 9.72%) remained different, however, and showed a slight increase to 117% and 118% of their original extensibilities, indicating some slippage of individual fibers in the yarns during the cycling procedure. The breaking load of the more elastic 50/1 yarn was practically unchanged by cycling, while that of the 12/1 yarn decreased from 833 to 726 g., revealing its insufficient resistance to fatigue. Both yarns had a similar recovery behavior after the cycling procedure, manifesting again the effect of mechanical conditioning. The relative value of permanent set at the breaking point was 20% for each yarn. The increase in recovery of the less elastic 12/1 yarn was thus markedly higher.

It can be summarized that mechanical conditioning eliminated the differences originally present in the two cotton yarns and that the 50/1 yarn was less affected by repeated extensions due to its higher elasticity. The 50/1 yarn has a higher "functional stability," if this expression can be used here as it has been by Quig [30] to denote the permanence in properties in some new synthetic fibers.

* The twist was 22.7 turns/in. (8.9 turns/cm.) for the 50/1 and 11.6 turns/in. (4.6 turns/cm.) for the 12/1 yarn, corresponding to twist multipliers of 3.21 and 3.28, respectively.

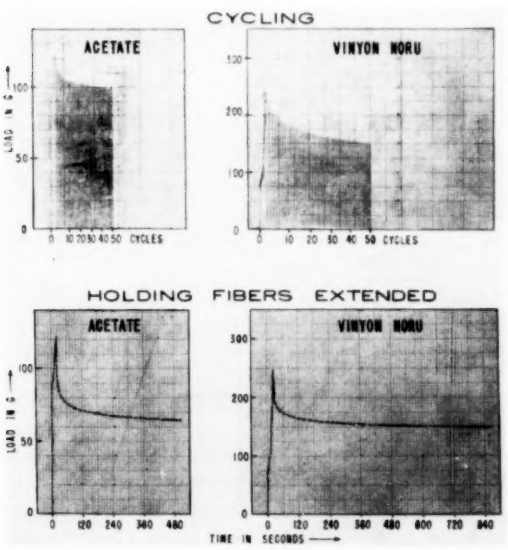


FIG. 9. *Mechanical conditioning by cycling and by holding fibers extended.*

Cycling and Sustained Extension

Fibers can be mechanically conditioned, not only by cycling, but also by holding them extended. Both procedures were followed in the mechanical conditioning of acetate and Vinyon NORU multifilaments. Each fiber was extended in 50 cycles to 80% of its extensibility as in the previous tests. Separate samples were also extended to the same elongation and held extended in the Instron tensile tester for twice the length of time necessary for performing the 50 cycles. Both procedures are depicted in the load-time plots of Figure 9. The test conditions and the average behavior of the fibers both originally and after mechanical conditioning (followed by 1 hr. relaxation) are shown in Table III and Figure 10.

A much longer time was necessary to perform the 50 cycles with Vinyon NORU than with acetate, not so much because of the higher actual strain to which Vinyon NORU was extended (24.2% compared to 19.5%) but rather because of its markedly higher elastic recovery at this level.

The load decay of acetate was less by cycling than by sustained extension. The Vinyon NORU showed practically no difference in this respect. The fiber length of both fibers increased in the two procedures more than expected from a single loading step (after immediate removal of the extension and 5 min. relaxation). The higher length increases and the re-

TABLE III. MECHANICAL CONDITIONING OF ACETATE AND VINYON NORU MULTIFILAMENTS BY CYCLING AND BY HOLDING THE FIBERS EXTENDED

	Acetate			Vinyon NORU		
	Original	Cycling (50 cycles)	Holding extended	Original	Cycling (50 cycles)	Holding extended
Conditioning elongation						
(% of original length)		19.5	19.5		24.2	24.2
(% of elongation at break)		80	80		80	80
Conditioning load[1]						
(g.)		122	122		245	247
(% of load at break)		88	88		79	80
Time of conditioning (sec.)		252	504		432	864
Load decay (g.)[1]		24	58		93	99
Load decay (% of the conditioning load)		20	48		38	40
Expected length increase (%)[2]		12.4	12.4		13.5	13.5
Observed length increase (%)[3,4]		16.9	15.3		16.2	15.0
Observed length increase (% of expected value)		137	124		120	111
Fineness (grex)	111	95.1[3]	96.2[3]	111	94.6[3]	96.4[3]
Elongation at break (%)	24.3[4]	6.0[5]	6.8[5]	30.3[4]	11.9[5]	13.7[5]
Load at break (g.)	139	150	147	310	321	329
Uncorrected tenacity at break (g./gx.)[6]	1.25	1.35	1.32	2.79	2.89	2.97

[1] Observed in individual tests shown in Figure 9.

[2] Calculated from the relative values of permanent set in a single loading step: 64% for acetate and 56% for Vinyon NORU at the conditioning strain.

[3] After 1 hr. relaxation.

[4] Correlated to the original fiber length.

[5] Correlated to the new fiber length and shown in Figure 10.

[6] Correlated to the original fiber fineness (111 gx.) and shown in Figure 10.

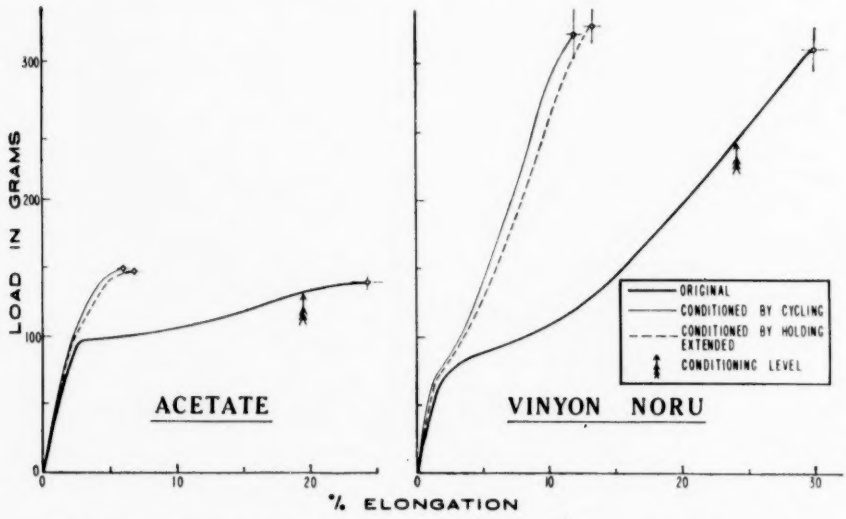


FIG. 10. *Load-elongation curves of acetate and Vinyon NORU multifilaments.*

duced new extensibilities after cycling reveal that the dynamic test (cycling) had a slightly greater effect than holding the samples extended. This is remarkable since cycled fibers were subjected to the maximum conditioning strain for a much shorter time. Dynamic tests are thus more efficient than static tests in mechanical conditioning to identical strain levels. A similar observation was made by Zart [39] in stretching different types of viscose staple fibers to an identical and constant stress level —*i.e.*, to 75% of their breaking load. Rupture always occurred in a surprisingly shorter time by

TABLE IV. PROPERTIES OF ACETATE MULTIFILAMENT AFTER MECHANICAL CONDITIONING

	Mechanically conditioned and tested:			
	Immediately	After 1 hr.	After 24 hrs.	Original
Length increase (%)[1]	17.8	16.9	15.6	—
Shrinkage during relaxation (%)[1]	—	0.9	2.2	—
Fineness (grex)	94	95	96	111
Elongation at break (%)	4.8[2]	6.0[2]	7.1[2]	24.3[1]
Coefficient of variation (%)	7.9	9.8	6.8	5.1
Load at break (g.)	152	150	147	139
Uncorrected tenacity at break (g./gx.)	1.37[3]	1.35[3]	1.32[3]	1.25
Coefficient of variation (%)	2.4	1.8	1.6	2.3

[1] Correlated to the original fiber length.
[2] Correlated to the new fiber length after mechanical conditioning.
[3] Correlated to the original fineness (111 gx.).

cycling than by permanent tension, showing the much higher effect of dynamic tests.

Alterations in Mechanically Conditioned Fibers

Immediately after mechanical conditioning, fibers are unstable, tending spontaneously to regain their original properties. In most cases, the restoration is limited but still noticeable, as demonstrated by the numerical data of mechanically conditioned acetate multifilament in Table IV. Immediately after 50 cycles to 80% of its extensibility, this fiber showed a length increase of 17.8%. Subsequently there was a spontaneous decrease in the fiber length by relaxation shrinkage accompanied, of course, by a slight increase in grex. After 1 hr. the length increase of the fiber was reduced to 16.9% and after 24 hrs. to 15.6% of the original length. The relaxation shrinkage could not occur without structural rearrangements within the acetate multifilament. These are manifested by the altered tensile properties. The extensibility of 4.8% immediately after cycling increased after 1 hr. and 24 hrs. to 6.0% and 7.1%, respectively. On the other hand, the fiber tenacity of 1.37 g./gx. immediately after cycling was reduced to 1.35 and 1.32 g./gx. An increase in extensibility and simultaneous decrease in tenacity during relaxation reflect diminishing orientation, or randomization, and approach to the status prevailing before mechanical conditioning.

The alteration of mechanically conditioned fibers appears to be enhanced by heat and by swelling, both of which facilitate structural rearrangements. This is shown by the data of Table V and the five stress-strain curves *A-E* in Figure 11 demonstrating the stress-strain relationship of the acetate multifilament after different treatments. If the mechanically conditioned fiber is heated to 212°F (100°C) for 4 hrs., considerable shrinkage occurs (3.8% of the original fiber length or 3.3% of the new fiber length). After this treatment, the fiber (under standard conditions of temperature and humidity) is only 13.1% longer than before conditioning.* Accordingly, the extensibility increases from 6.0% to 8.9%, and the tenacity decreases from 1.35 to 1.27 g./gx. The stress-strain curve of the heated sample, *C*, has an intermediate position between curves *B* and *A*, demonstrating the trend of the fiber to regain its original behavior.

The influence of swelling in water is similar, causing even higher shrinkage of the mechanically conditioned fiber (4.6% of the original or 3.9% of the new length) connected with a further increase in extensibility (to 16.2%) and a reduction in tenacity (to 0.63 g./gx.) if tested wet. The stress-strain curve of the mechanically conditioned fiber in the swollen state (*D*) is similar but still different from that of the original fiber when wet (*E*). After mechanical conditioning the plasticizing action of water is less pronounced than originally where it is evidenced by high extensibility and also by decreasing tenacity values after the yield point is exceeded.

Heat treatment and swelling also make the recovery of the mechanically conditioned acetate similar to that of the original fiber. This is apparent from the actual and relative values of elongation components listed in Table V and from the five quadratic graphs *A–E* shown in Figure 12. The recovery behavior of these same five acetate samples *A–E* is demonstrated here by relative values of the three elongation components plotted against percentage of extensibility. Demonstrating the recovery of different samples by

* Heat treatment (under the same conditions) of acetate multifilament in the original state had practically no influence on the fiber length and the stress-strain curve.

TABLE V. STRESS-STRAIN AND RECOVERY DATA OF ACETATE MULTIFILAMENT AT THE BREAKING POINT AFTER DIFFERENT TREATMENTS

	Elongation at break (%)	Load at break (g.)	Uncorrected tenacity at break[2] (g./gx.)	Elongation components (%) Actual values Recovery Immediate elastic	Delayed	Permanent set	Relative values Recovery Immediate elastic	Delayed	Permanent set	Increased length[1] (%)	Shrinkage during treatment[1] (%)
A Untreated	24.3[1]	139	1.25	3.4	3.9	17.0	14	16	70	0	—
B Mechanically conditioned[3]	6.0[4]	150	1.35	2.6	2.9	0.5	44	48	8	16.9	—
C Mechanically conditioned and heated 4 hrs. to 212°F (100°C)[5]	8.9[4]	141	1.27	2.5	3.6	2.8	28	41	31	13.1	3.8
D Mechanically conditioned and swollen in water	16.2[7]	70	0.63	2.0	4.0	10.2	12	25	63	12.3[6]	4.6[6]
E Original swollen in water	29.8[1]	774	0.66	2.6	4.2	23.0	9	14	77	−1.0[6]	1.0[6]

[1] Correlated to the original fiber length.
[2] Correlated to the original fineness (111 gx.).
[3] After 1 hr. relaxation.
[4] Correlated to the length after the treatment.
[5] Tested at 70°F (21.2°C).
[6] After drying.
[7] Correlated to the dry length after mechanical conditioning.

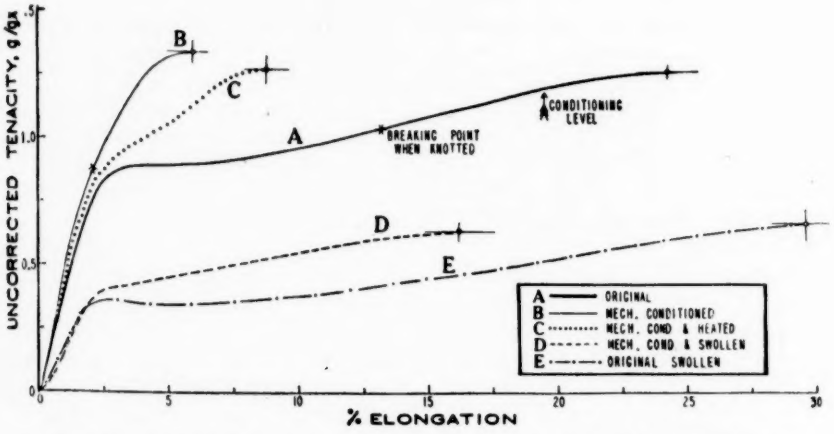


FIG. 11. *Stress-strain curves of acetate multifilament after different treatments.*

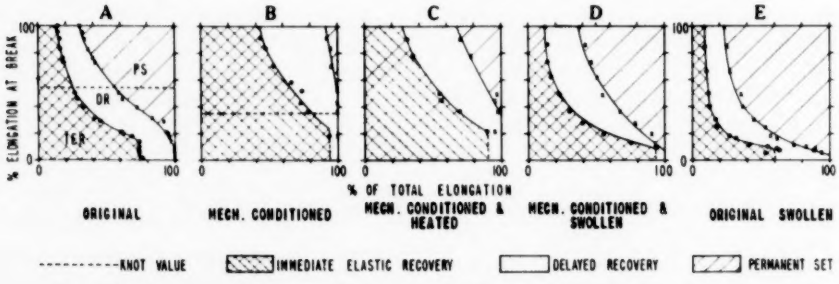


FIG. 12. *Recovery behavior of acetate multifilament after different treatments.*

TABLE VI. KNOT BEHAVIOR OF ACETATE MULTIFILAMENT

	Before mechanical conditioning	After mechanical conditioning*
Elongation (%)		
Without knot	24.3	6.0
With knot	13.2	2.1
Relative knot value	54%	35%
Tenacity (g./gx.)		
Without knot	1.25	1.35
With knot	1.04	0.87
Relative knot value	83%	65%

* Elongation is correlated to the new fiber length after mechanical conditioning and tenacity to the original fineness (111 gx.).

equal quadrates permits an easy comparison of their recovery behavior despite the considerable differences in their extensibilities. The five graphs clearly show that the high permanent set of the original fiber (*A*) almost disappears after mechanical conditioning (*B*) and returns progressively after heat treatment (*C*) and swelling (*D*), although the high "plasticity" of the original fiber when swollen in water (*E*) is not entirely attained.

Mechanical conditioning not only influences the tensile behavior of fibers, but also affects transverse properties such as bending, torsion, and shear, mostly in an undesirable sense. This is apparent from the lower knot values after mechanical conditioning shown in Table VI.* Before conditioning the extensibility and tenacity of knotted acetate are 54% and 83%, respectively, of the original values. After mechanical conditioning, however, the corresponding values diminish to 35% and 65%, showing a marked weakening of the fiber perpendicular to the fiber length.

Stress Hardening and Fatigue by Mechanical Conditioning

After mechanical conditioning a slight stiffening and strengthening (in the direction parallel to the fiber length) of the acetate multifilament was observed, and this was demonstrated in Figure 2. The initial modulus increased from 37 to 46 g./gx. and the average breaking load from 139 to 150 g. according to Table I. This is apparently the result of orientation or alignment of long-chain molecules in the

* The breaking point of knotted fibers is also demonstrated on the stress-strain curves of Figure 11 and on the quadratic graphs of Figure 12.

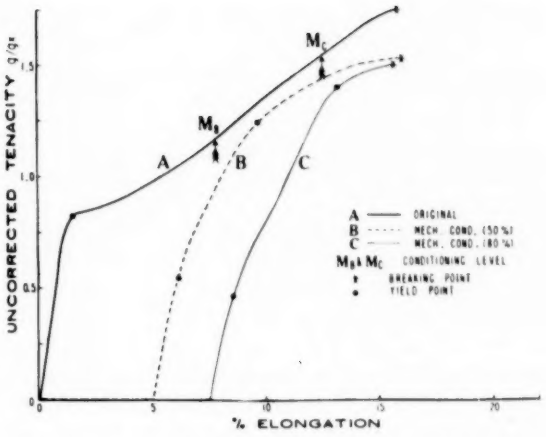


FIG. 13. *Stress-strain curves of viscose multifilament.*

fiber length, known also as "stress hardening." In contrast to the behavior of acetate, a weakening and a diminished initial modulus of viscose was demonstrated in Figure 2 and Table I after mechanical conditioning. The average breaking load decreased from 195 to 167 g. and the initial modulus from 69 to 55 g./gx. Figure 13 shows the stress-strain curves of viscose multifilaments originally (*A*) and after mechanical conditioning (in 50 cycles) to 50% of the extensibility (*B*) and to 80% of the extensibility (*C*). The presentation here deviates from that used previously. Tenacity and elongation values of the curves are correlated to the original fiber fineness and fiber length, respectively, as demonstrated in curve *II* of Figure 5A. The initial horizontal part on the curves after mechanical conditioning reflects the permanent set attained by cycling, which was 5.0% at the lower and 7.5% at the higher conditioning level. The new extensibility (correlated to the new fiber length) was 10.6% at the lower and 7.7% at the higher conditioning level. Nevertheless, the over-all extensibility * (16.2% and 15.8%) remained in both cases practically identical to the original extensibility of 15.7%. The uncorrected tenacity is markedly diminished, however, after cycling from 1.75 to 1.52 and 1.51 g./gx.† The initial modulus decreases, and, instead of a distinct yield point, two less pronounced yield points appear after conditioning, one at the

* The sum of permanent set and new extensibility, both correlated to the original fiber length.

† The breaking load and the corrected tenacity diminished also (from 195 to 169 and 167 g. and from 2.02 to 1.76 and 1.75 g./gx., respectively).

beginning and one at the end of each stress-strain curve. The first yield point is analogous to that of the original fiber, although it has lower tenacity values as the conditioning level increases. The second yield point increases, however, with the conditioning level and indicates (at least approximately) the beginning of the "unaltered" portion of the original stress-strain relationship. A similar weakening of fibers by repeated strain, as demonstrated here for viscose, is known as "fatigue" and is not exceptional. It may occur in any textile fiber extended close enough to the breaking point.

Stretching alters the properties of fibers, increasing their anisotropy as a result of structural rearrangements known as "orientation." Orientation occurs in the amorphous part as well as in the crystalline part of fibers without decisively influencing the amount of the crystalline portion. This behavior is in contrast to the orientation and simultaneous crystallization of natural rubber and of some rubber-like substances (polychlorobutadiene, polyisobutylene) when stretched. In these materials the orientation and crystallization due to stretching disappear after the tension is released. In textile fibers, however, the orientation remains to a great extent if the elastic limit has been exceeded, and new properties are permanently imparted to the fibers. Besides increased fiber length, diminished extensibility, and enhanced elasticity, the increased tenacity is the best-known alteration observed on oriented fibers. The tenacity of stretched viscose, acetate, and man-made protein and synthetic fibers increases with orientation up to a certain limit. Beyond this limit, the tenacity remains unaltered by further stretching and can even decrease, as it does in "overstretched" fibers. Stretching of fibers might also cause slippage of long-chain molecules, breaking cross-bonds. It can result in cracks and deterioration of the crystal lattice, as was observed on nylon by Bergmann, Fankuchen, and Mark [2], and by Kauffman and George [20]. These structural changes may affect the tensile properties of fibers adversely, and they are responsible for the fact that the breaking load of fibers increases only up to a certain degree of orientation.

The systematic investigation of the stretching mechanism of viscose and cuprammonium rayon revealed that stretching has no influence on the form and magnitude of the crystallites in these fibers. It markedly affects, however, the position of the crystallites in relation to the forces causing the deformation and to the dimensions of the sample.* According to Sisson [31], the crystallites of cellulose *II* possess a major orienting tendency with reference to the [010] axis and a minor selective orienting tendency in reference to the (101) planes. Their response to stretching consists in alignment of the long-chain molecules with their axis—[010] direction of the crystal lattice—parallel to the fiber length, and in turning the (101) plane (held together by hydrogen bonds) into preferential positions perpendicular to the fiber radius. The alignment of crystallites parallel to the fiber length is known as "axial orientation" and the preferential position of the (101) planes perpendicular to the fiber radius as "planar orientation." Both are due to the plate-like shape of crystallites, and they are revealed by the x-ray patterns of stretched cellulose fibers. The axial orientation can be determined quantitatively either from the difference in the azimuthal length of the 101 and 101 paratropic (equatorial) interferences according to Hermans, Hermans, Vermaas, and Weidinger [11, 12], or more conveniently from the length of the 020 diatropic (meridional) interference using the method of Kast and Prietzschk [12, 18] described in further detail in the publications of these authors. The planar orientation is obtained from the azimuthal length of the 101 paratropic interference, a widely used technique to determine the "orientation" in cellulose fibers. The degree of axial and planar orientation can vary greatly according to the conditions under which the stretching is performed. Both orientations and, of course, also the ratio between them affect the mechanical properties of fibers. Contrary to the axial orientation, which strengthens the fiber in the direction of fiber length, the planar orientation is connected with internal stresses. These are manifested in the decrease of extensibility and in the deterioration of fiber quality. Obviously, turning crystallites into the direction of the fiber axis can be achieved more easily than turning a plane into a preferential position, and without destruction of the crystalline order.

Kast [16, 17] demonstrated that both orientations, axial and planar, increase when cuprammonium rayon is stretched while still swollen in an early stage of the fiber-forming process. They give enhanced tenacity and extensibility in the end-products, increasing the work absorption and consequently the fiber qual-

* Orientation of viscose can occur by shrinkage as well as by extension.

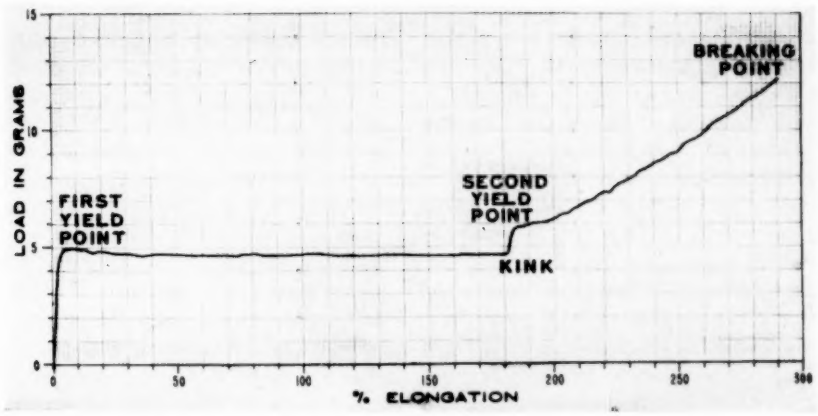


FIG. 14. *Load-elongation curve of undrawn Dacron.*

ity. The planar orientation prevails, however, in producing viscose rayon and also when deswollen cuprammonium filaments are stretched. The planar orientation is even more predominant if dried viscose filaments are extended, causing a detrimental effect on the fiber properties, as shown in Figure 13. Contrary to this behavior, in stretching acetate fibers mainly axial orientation occurs without deteriorating the fiber quality. The planar orientation is less pronounced here due to the acetyl groups, higher plasticity, and lower crystallinity of cellulose acetate [13] compared to the cellulose *II* present in viscose rayon.

"Cold-Drawing" of a Dacron Monofilament

It is not necessary to extend fibers 50 times to a high conditioning level in order to change their properties considerably. Mechanical conditioning will occur even in a single step if the material is susceptible to such alterations after a deformation. This can be demonstrated by undrawn Dacron, a highly extensible fiber whose excessive permanent set—91% of the total elongation at the breaking point—prohibits its practical use as a textile material.

Undrawn Dacron was investigated in the form of single filaments having an average fineness of 16.6 grex, 292% elongation, and 12.2 g. load at break, corresponding to an uncorrected tenacity of 0.74 g./gx. or a corrected tenacity of 2.90 g./gx. The fiber tenacity was thus considerably lower than that of commercial Dacron polyester fibers, whose corresponding tenacity values are 5.28 and 6.25 g./gx., respectively (Table I).* Although not observable on x-ray patterns (Figure 17A), a slight orientation may be present in the undrawn fibers investigated due to the extruding process. The fiber has a peculiar stress-strain relationship, shown by the load-elongation curve in Figure 14.* It is characterized by two distinct yield points separated from each other by a long horizontal portion. Up to the first yield point (4% strain, 4.9 g. stress) the behavior of the fiber is not unusual. The horizontal portion, beginning at the first yield point, indicates high plastic flow and necking. The filament can be elongated from 4% to approximately 182% while the tension slightly decreases until a kink in the stress-strain curve appears. Here the tension increases suddenly from 4.6 to 5.8 g. within 2%–4% elongation until the second yield point is reached. The end part of the load-elongation curve is approximately linear, is fairly steep, and reveals some stress hardening.

Similar is the stress-strain curve of undrawn Perlon U (polyurethan, addition-product of hexamethylene diisocyanate and 1,4-butanediol) [4]. In extending undrawn Perlon U monofilaments a decrease in tension and a long horizontal portion is observable after the first yield point. At 220% elongation, after the necking has been terminated, an essential increase in tension occurs within a few percent elongation. This pronounced kink in the stress-strain relationship is then followed by the relatively short and only moderately steep end portion of the curve (Figure 1 of [4]).

* Only corrected tenacities should be compared.

* Loads (tensions) in grams are demonstrated here because uncorrected tenacities (g./gx.) would be misleading in view of the high extensibility.

Due to its considerable plastic flow (evidenced by high permanent set), undrawn Dacron is very suitable for demonstrating the alterations which may occur when a fiber has been extended. Six individual samples were elongated to progressively increasing elongation levels *A*, *B*, *C*, *D*, *E*, and *F*, marked on the simplified load-elongation curve of Figure 15: *A*, up to the first yield point; *B*, *C*, and *D*, between the first yield point and the kink on the horizontal portion; *E* and *F*, above the second yield point. The tests, using a 5.0-in. (12.7 cm.) gage length and a jaw separation corresponding to 100% elongation per minute, were made in the following steps: (*1*) first loading and recovery cycle to predetermined strain level, followed by relaxation in tester without tension for 5 min.; (*2*) second loading and recovery cycle to previous strain level; (*3*) rupture of mechanically conditioned fiber (without any relaxation). The first and second loading cycles and the final load-elongation curves (after mechanical conditioning) are represented in a simplified way in Figure 15. Elongation values are always correlated here to the initial length. The second cycle and the final curves are shown with the omission of the permanent set obtained in the first cycle. The demonstration of the final stress-strain relationship is analogous, therefore, to that of curve *II* in Figure 5A. Numerical data of these tests are listed in Table VII.

The following facts are revealed by this mechanical conditioning procedure, which is basically identical to the "cold-drawing" of Dacron to increasing strain levels: An extension up to the first yield point, *A*, has practically no effect on the tensile properties. The second cycle is identical to the first, and the final load-elongation curve remains practically unchanged. It has an unaltered first yield point, a large horizontal portion ending with the kink, a second yield point, and a fairly steep end portion. Rupture occurs at approximately the same point as for the original fiber. Deviations here are mainly due to the unevenness of the material tested, which was considerable.

If the fiber is extended above the first yield point but below the kink (*B*, *C*, and *D*), a marked change in tensile properties occurs up to the point to which the fiber was extended. This is already revealed in the second cycle, from which the horizontal portion reflecting necking disappears. The final load-elongation curves demonstrate that an additional yield point, "the new lower yield point," appears (at 2.4 g. load and at 2.2%–2.9% elongation). The stress value of this new yield point is independent of the straining history, while its elongation value seems to increase slightly at higher conditioning levels. The first yield point of the original fiber remains unaffected. The horizontal portion beyond this yield point is diminished, however, by the amount of permanent set eliminated in the first cycle and it still indicates necking. That part of the curve which exceeds the conditioning level *B*, *C*, or *D* remains almost unchanged. It contains the rest of the horizontal portion with the kink, the unaffected second yield point, and the steep end portion of the original curve. The elongation at break is, of course, markedly diminished if the permanent set obtained in the first cycle is not taken into account.

Entirely different fiber characteristics are revealed after extensions to points *E* and *F*, exceeding the second yield point. This is shown not only by the marked differences between the first and second loading cycles, but also by the final load-elongation curves. The two original yield points disappear. The "new lower yield point" remains almost unaffected, and, instead of the second yield point of the original curve, a "new upper yield point" is observed. Contrary to the "new lower yield point," neither its stress nor its strain value is constant, and both definitely increase with higher extension level. The end portion of the original curve above the conditioning level (points *E* and *F* in Figure 15) remains almost unaffected here, too. The new extensibility is, of course, very much diminished if the permanent elongation attained in the first cycle is not taken into account.

The over-all extensibility (Table VII) slightly exceeds the original elongation at break, indicating some additional slippage during the procedure performed in comparison to the extension in a single step. The load at break seems to increase somewhat as a result of stress hardening by orientation.

It is interesting to note that the specimen extended fairly close to the breaking point (to point *F* in Figure 15) is similar in extensibility to commercial Dacron polyester fibers. The "cold-drawn" fiber has an extensibility of 22% (correlated to the new length after mechanical conditioning) and a breaking load of 15.1 g., corresponding to 0.91 g./gx. uncorrected tenacity when correlated to the original grex, 3.20 g./gx. when correlated to the decreased grex after conditioning, and 3.91 g./gx. corrected tenacity. The two load-elongation curves shown in Figure 16 re-

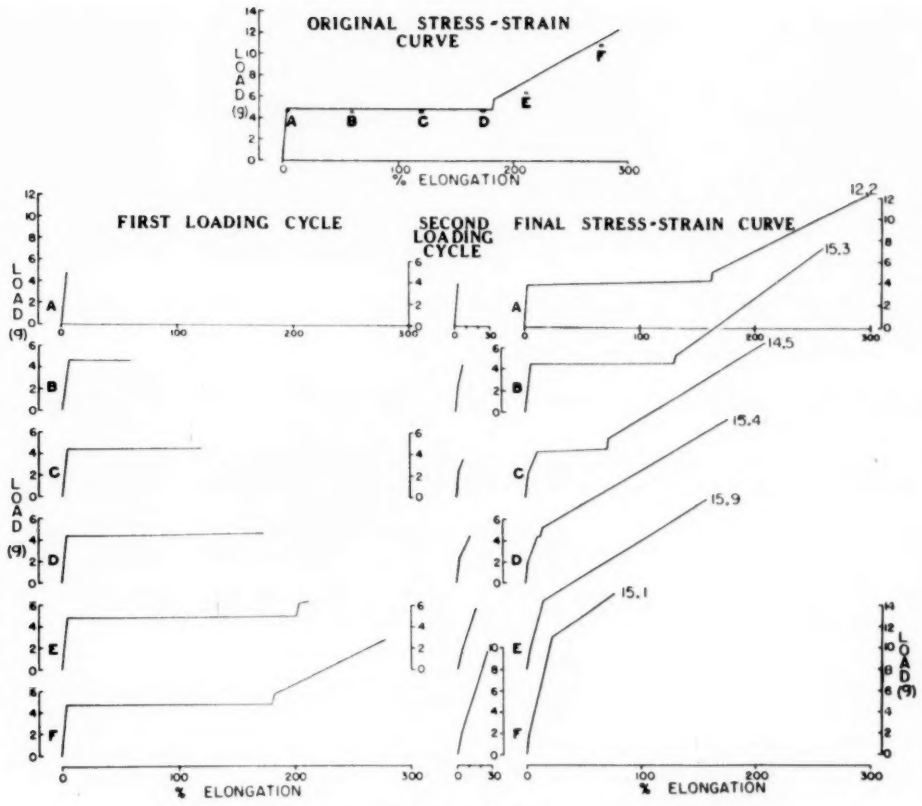


FIG. 15. *Effect of mechanical conditioning on undrawn Dacron.*

TABLE VII. EFFECT OF MECHANICAL CONDITIONING ON UNDRAWN DACRON

	Extension level	First cycle: Elongation % of original length[1]	First cycle: Elongation % of ultimate value (292%)	First cycle: Load (g.)[1]	First cycle: Load % of ultimate value (12.2 g.)	Second cycle: Permanent elongation (% of original length)	Final stress-strain curve after mechanical conditioning: Elongation at break % of original length[1,2]	Elongation at break % of "new" length	Elongation at break % of original length[3] (over-all extensibility)	Load at break[1] (g.)
A	Below the first yield point	3	1	4.1	34	0	300	300	300	12.2
B	Between the first	60	21	4.6	38	52	260	171	312	15.3
C	yield point and	120	41	4.6	38	114	209	98	323	14.5
D	the kink	174	60	4.7	39	163	176	67	339	15.4
E	Above the second	212	73	6.4	52	196	167	56	363	15.9
F	yield point	278	95	10.8	89	252	77	22	329	15.1

[1] Data demonstrated in Figure 15.
[2] Without the permanent elongation observed in the second cycle.
[3] Including the permanent elongation observed in the second cycle.

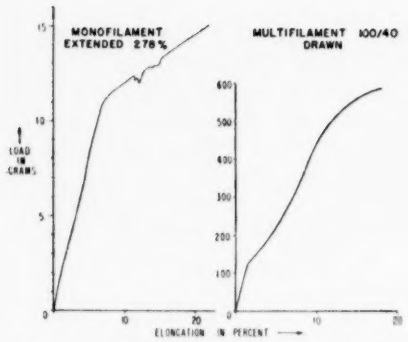


FIG. 16. *Load-elongation curves of Dacron fibers.*

veal, however, considerable differences in their stress-strain relationship. This is most likely due to the fact that the "cold-drawn" specimen is markedly less crystalline and less oriented than commercial Dacron polyester fiber.

According to the x-ray pattern (Figure 17A) the undrawn Dacron filaments investigated are amorphous, without noticeable orientation. An orientation without significant crystallization occurs, however, during the mechanical conditioning procedure, as demonstrated by the x-ray patterns of Figure 17D, E, and F. The fibers extended below (D) and above (E) the kink are oriented, and they have essentially identical x-ray diagrams. The unconventional raise in tension (the kink on the curve) after the necking has been terminated must therefore have its origin in structural changes other than sudden crystallization or orientation of crystallites. Although the highly extended filament (F) is oriented, it has poor crystallinity. Its diffuse x-ray diffraction pattern with very broad equatorial spots is somewhat similar to the x-ray diagrams of highly stretched acetate rayon.* It is markedly different from that of a commercial Dacron polyester fiber (Figure 18), which reveals good crystallinity as well as high orientation.†

The structural changes of Dacron due to mechanical conditioning (cold-drawing) have some permanence since they are manifested even after a heat treatment and considerable shrinkage. If the undrawn Dacron fiber tested is heated to 302°F (150°C) for 1 hr., shrinkage of about 37% occurs as a result of recrystallization. The good crystallinity is revealed by the x-ray pattern (Figure 19, I). The fiber loses its plastic flow entirely, it becomes elastic, and consequently it cannot be drawn. It is brittle, the elongation at break being only 4% (Figure 20, I). If samples extended to 150% or 270% are heat-treated in a similar way, reduced shrinkage (32% and 15%, respectively) is observed, and the extensibility increases to 40% and 52%, respectively. The load-elongation curves of these heat-treated Dacron fibers are shown in Figure 20, II and III, and their x-ray

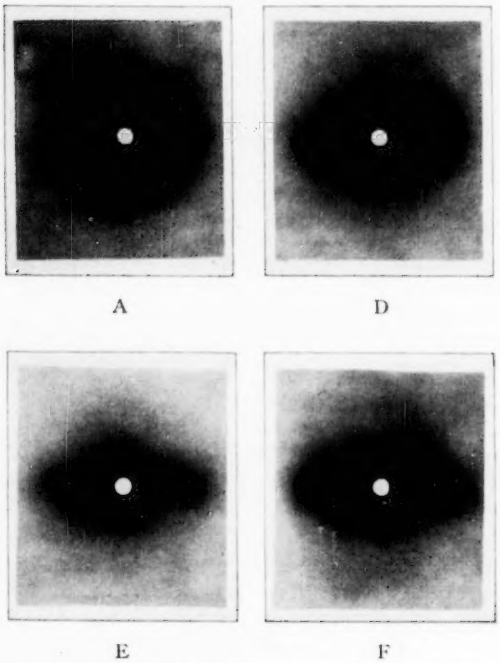


FIG. 17. *X-ray diffraction patterns of Dacron monofilaments.* A—*Undrawn.* D—*Extended below the kink (174%).* E—*Extended above the kink (212%).* F—*Extended close to rupture (278%).*

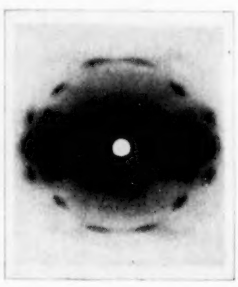
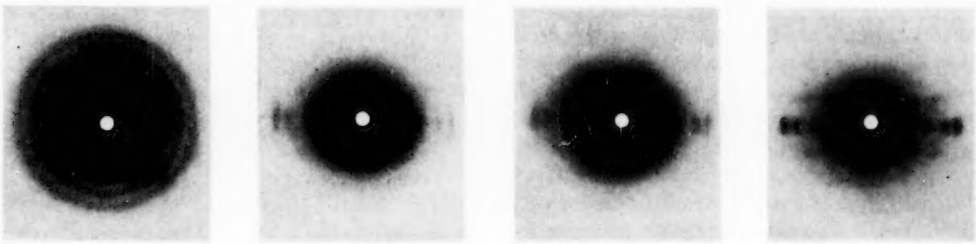


FIG. 18. *X-ray diffraction pattern of Dacron multifilaments 100/40.*

* Figure 17 in [13].
† Figures 45a and b in [13].



I II III IV

FIG. 19. *X-ray diffraction patterns of Dacron fibers after heat treatment.* I—*Monofilament undrawn (shrinkage, 37%).* II—*Monofilament extended 150% (shrinkage, 32%).* III—*Monofilament extended 270% (shrinkage, 15%).* IV—*Multifilament drawn (shrinkage, 7%).*

patterns in Figure 19, II and III. These diagrams reveal increased crystallinity if compared with those of similar fibers before heat treatment (D and F in Figure 17) as a result of recrystallization and a fairly good orientation of crystallites, too. The orientation is surprising in view of the considerable contraction during the heat treatment, since shrinkage generally causes randomization (disorientation) in fibers. It is analogous to the behavior of cold-drawn polyurethan (Perlon U), polycaprolactam (Perlon L), and polyhexamethylenesebacamide (6,10-nylon) fibers after heat treatment. Brenschede [4] observed enhanced orientation and sometimes even increase in fiber length of stretched polyurethan fibers after "annealing" (heat treatment) at 302°F (150°C). Based on birefringence and x-ray diffraction studies he interpreted the phenomenon as formation of aligned crystallites from preoriented noncrystalline domains.

The crystallinity and orientation of highly drawn Dacron fibers after heat treatment are still considerably lower than those of commercial Dacron fibers. It must be mentioned that the heat stability of commercial Dacron multifilaments is rather good. If they are heat-treated—302°F (150°C) for 1 hr.—only slight shrinkage (7%), almost no alteration of the stress-strain curve (Figure 20, IV), and no noticeable change of the x-ray diffraction pattern (Figure 19, IV)* occur. It is also interesting to note that if undrawn Dacron monofilament is extended close to the breaking point (270%) and heat-treated, its stress-strain curve (Figure 20, III) is similar in character to that of a commercial Dacron multifilament with two yield points. Marked differences exist, however, in the extensibility and tenacity of these samples, as would be expected from their structural differences. The extensibility of the cold-drawn monofilament is 52% (after heat treatment) and the corrected tenacity (the uncorrected tenacity is not comparable) is 3.80 g./gx., while the corresponding data of the heated Dacron multifilament are 20% and 5.55 g./gx., respectively.

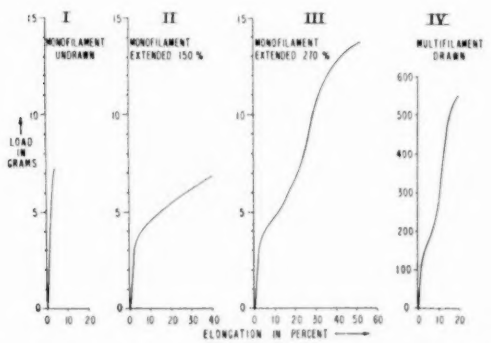


FIG. 20. *Load-elongation curves of Dacron fibers after heat treatment.*

Summarizing, it can be stated that considerable alterations of undrawn Dacron filaments occur after an extension if the conditioning (drawing) level exceeds the first yield point. These consist of an increase in fiber length by permanent set (mostly due to necking) and, consequently, of reduced new extensibility. Instead of the two original yield points, two new yield points appear successively on the stress-strain curves. Only the higher yield point is markedly influenced by the previous straining history. Stretching causes a slight (if any) stress hardening, and it seems to increase the over-all extensibility.

* The insignificant differences between the diagrams of Figures 18 and 19, IV, are mainly due to differences in the geometrical dimensions of the samples and in their exposure to the x-ray beam.

These alterations are due to structural changes during stretching to which new structural rearrangements (crystallization, orientation) are added by heat treatment.

Similar observations were made by Boehringer [3] in the drawing of Perlon L. This fiber is extended in the ratio 1:40 during the fiber forming (spinning) procedure and then again in a separate drawing step in the ratio 1:5. Therefore, a total stretching in the ratio 1:200 occurs, starting from the length at the spinneret. The increase in density is very slight, if any, during the drawing process.* The initial modulus, the yield point (stress and strain at the elastic limit), the breaking strength, and the relative values of elastic recovery † ("degree of elasticity") at the breaking point increase substantially. The breaking load remains, however, almost unaffected. The extensibility, the actual values of elastic recovery † at the breaking point, and the total work of rupture decrease in the drawing procedure. It must be noted that the recoverable work ‡ increases first and then decreases later. A maximum elastic energy (work) was observed at drawing ratios between 1:2.8 and 1:4.2, indicating the limit to which Perlon L. fibers could be drawn under the particular conditions without being overstretched.

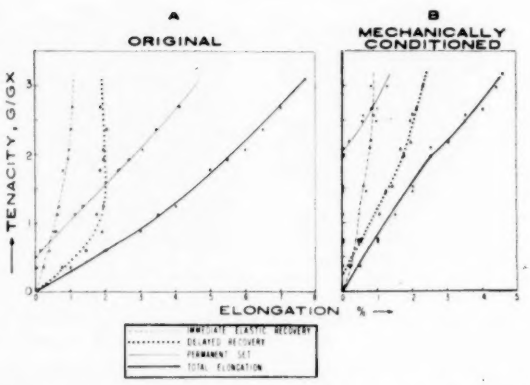


FIG. 21. *Elongation components of 56/3 cotton thread demonstrated by four curves.*

Mechanical Conditioning of a Cotton Thread

The behavior of a 56/3 cotton sewing thread after repeated stresses was different to some extent from that of the fibers discussed previously. Mechanical conditioning of this fiber is of practical interest since similar cotton threads are subjected to frequent stresses and strains at high speed in the sewing operation.

The actual fineness of the thread investigated was 298 grex. It had a twist of 23.8 turns/in. (9.4 turns/cm.) and a concave stress-strain relationship (demonstrated in curve *A* of Figure 25), with a work

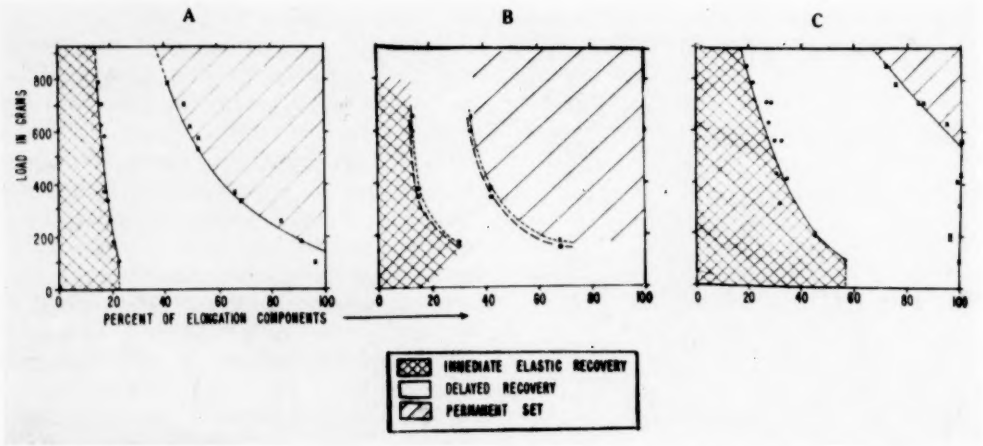


FIG. 22. *Elongation components of 56/3 cotton thread demonstrated by rectangular graphs.*

* No increase of density was detected by Brenschede [4] during drawing of Perlon U up to the ratio 1:4.5, whether the stretching was performed at 77°F (25°C) or at 338°F (170°C). The density increased however, from 1.182 to 1.218 after "annealing" at 338°F (170°C) due to recrystallization. The melting point of Perlon U is 361°F (183°C).

† Elastic recovery is the sum of immediate and delayed recoverable elongation.

‡ Recoverable or elastic work is the sum of the immediately recoverable work and creeping recoverable work.

factor of 0.42.* The elastic limit (yield point) is low at 0.5 g./gx. tenacity and 1.5% elongation,† the extensibility is 7.7%, and the breaking load 925 g., corresponding to 3.10 g./gx. uncorrected tenacity or 3.34 g./gx. corrected tenacity. The total work necessary to rupture is 10.6 g.-cm./gx. for 1 m. fiber length. According to the low elastic limit, the permanent set (secondary creep) of the thread is considerable, indicating that marked changes can be expected after extensions even to comparatively low stress or strain levels.

The recovery behavior of the thread is demonstrated by four curves (Figure 21A) representing the actual values of elongation components and also by a rectangular graph (Figure 22A) where relative values are plotted against load in grams. Data of these graphs were obtained in a single loading step using a relaxation time of 5 min. They demonstrate that the permanent set starts at the beginning of the stretching procedure and increases steadily up to the breaking point. Here the predominant part of the elongation does not recover, the actual and relative values of permanent set being 4.7% and 61%, respectively.

The thread was mechanically conditioned by extending separate samples repeatedly to the constant strain levels of 2%, 4%, and 6% elongation.‡ This was done in order to obtain the response of the thread to a low, a medium, and a relatively high strain.

The cycling technique is depicted in Figure 23 for the conditioning level of 6%. A 10-in. (25.4 cm.) specimen was extended first in 20 cycles between zero tension and 6% elongation at a jaw speed corresponding to 20% extension per minute. These cycles were recorded at a low chart speed. It can be seen that only the first cycle is significantly different from the following ones. Fairly constant cycles were obtained at about the tenth cycle, and a load decay from 604 to 553 g. occurred during the cycling operation. After 20 cycles the thread was allowed to relax for 5 min. in the Instron tensile tester. It was then extended again in two consecutive cycles from the original gage length to the previous elongation of 6% at the same jaw speed. These two cycles (21st and 22nd) were recorded at a chart speed ten times higher than previously in order to obtain a resolution suitable for the separation of the three elongation components. The 21st and 22nd cycles thus appear magnified in comparison to the first 20 cycles. The 21st cycle reveals a slight load recovery, from 553 to 562 g., considerable permanent set, 4.0%, and 1% immediate elastic recovery (obtained by extrapolation of the linear part on the recovery curve). The delayed recovery is consequently 1.0%. This latter elongation component is also evidenced by the noticeable difference between the recovery curve of the 21st cycle and the subsequent loading curve of the 22nd cycle. After the 22 cycles the thread was extended until rupture occurred. The final stress-strain curve was recorded at a diminished (1 : ½) load sensitivity without changing the previous jaw and chart speeds. Instead of the original concave stress-strain relation-

* A gage length of 10 in. (25.4 cm.) and a jaw speed of 20% extension per minute were used in testing this cotton thread. These conditions were preferable to those usually used in view of the relatively slow response of the Instron tensile tester.

† The elastic limit was obtained by the analysis of the stress-strain curve, as shown in Figure 21A.

‡ Ten individual samples were extended in each case to obtain the average behavior.

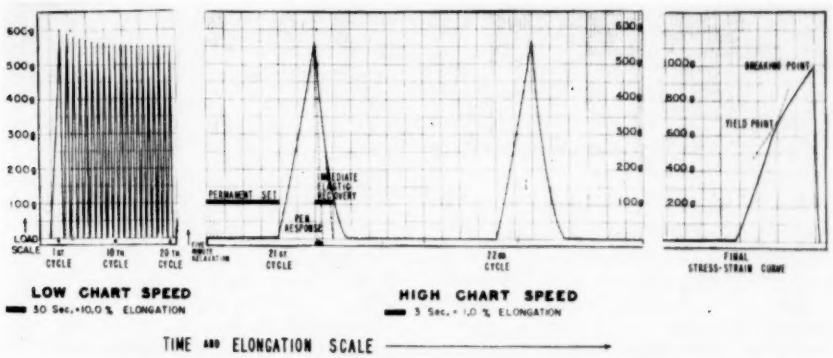


FIG. 23. *Cycling technique used in mechanical conditioning of 56/3 cotton thread.*

TABLE VIII. ALTERATION OF THE YIELD LOAD OF 56/3 COTTON THREAD AFTER MECHANICAL CONDITIONING

	A	*B*	*C*
		Mechanically conditioned	
	Original	Tested after 5 min. relaxation	Tested after 12 hrs. relaxation
1. Conditioning load (g.)			
a. Initial (1st cycle)		220	215
b. Ultimate (20th cycle)		202	198
2. Load decay (g.)		18	17
3. Yield load (g.)	145	265	234
4. Difference between (3) and (1*a*) (g.)		45	29
5. Breaking load (g.)	870	985	880

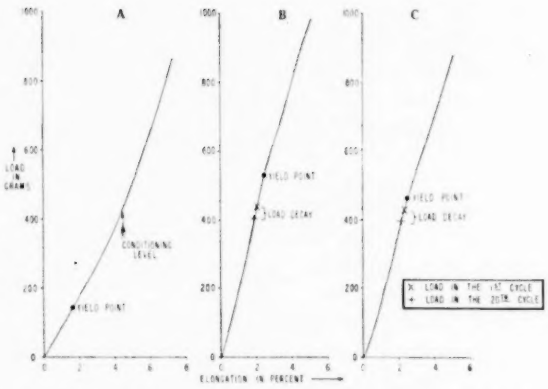


FIG. 24. *Alteration of the yield point during relaxation.*

ship (Figure 21A), a convex stress-strain curve * was obtained, with a work factor of 0.59 and a pronounced yield point fairly close to the breaking point. It will be noted that the yield load (670 g.) on the curve is higher than the conditioning load whether the initial stress (604 g. in the first cycle) or the ultimate value (503 g. in the 20th cycle after load decay) is considered as conditioning stress.

The yield point of mechanically conditioned fibers depends upon the previous stretching history, and it increases in most cases with higher conditioning level. It generally indicates that point where the alteration of the stress-strain relationship (due to stretching) ends and the original behavior starts to become apparent. The yield point of mechanically conditioned fibers is by no means constant; it is altered during relaxation. Therefore, the yield load of conditioned fibers can deviate more or less from the conditioning stress. This behavior is demonstrated by Figure 24 and Table VIII. The load-elongation curves of three individual specimens of the cotton thread are shown: (*A*) before mechanical conditioning; (*B*) and (*C*), after mechanical conditioning to the same constant elongation level of 4.5% † with the difference that (*B*) was tested after 5 min. and (*C*) after 12 hrs. relaxation. The conditioning stresses (loads corresponding to 4.5% strain in the 1st and 20th cycle) are marked on the curves *B* and *C* to better demonstrate the deviation of the yield load from these load values. It can be seen that the yield stress after mechanical conditioning exceeds the conditioning stresses (whether the higher or lower load value are taken into consideration) and that the difference between them diminishes upon relaxation * (line 4 in Table VIII).

The average stress-strain curves of the cotton thread after the cycling procedure to 2%, 4%, and 6% elongation levels are demonstrated in Figure 25B, C, and D.† A significant alteration of the original stress-strain relationship appears even at the lowest conditioning level (2%), which only slightly exceeds the original yield strain (1.5%). Very distinct yield points appear on the curves at increasing tenacity and elongation values with higher conditioning levels. The response of this cotton thread to repeated strains is thus different from that of most other textile fibers which generally have (as shown in Figure 6 and 7) less pronounced yield points after mechanical conditioning than originally. The stiffness (initial modulus) of the thread increases, too, with higher conditioning level, while the new extensibility and the work necessary to rupture markedly diminish without significant alteration of the breaking tenacity and breaking load.

In the cycling procedure (performed as shown in

* The presentation of the stress-strain curve corresponds to that of curve *II* in Figure 5A.

† Cycling was performed here on 15-in. (38.1 cm.) specimens at a jaw speed of 33% extension per minute in 20 cycles.

* In performing such tests with a similar cotton thread having less pronounced visco-elastic behavior, the yield load of the mechanically conditioned thread almost reached the initial conditioning stress value after 12 hrs. relaxation.

† Uncorrected tenacities are correlated here to the new grex, and elongation values to the original fiber length. The fiber grex after cycling differs little from the original since no marked increase of the fiber length was observed after the cycling operation. The length increases were only 0.7%, 2.3%, and 4.0%, respectively, for the conditioning levels of 2%, 4%, and 6%.

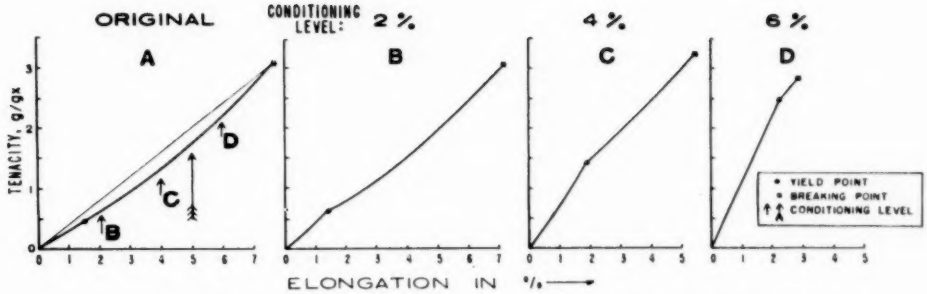


FIG. 25. *Response of 56/3 cotton thread to repeated extensions.*

Figure 23) a higher portion of the elongation became unrecoverable than after a single extension. This is demonstrated by the rectangular graphs of Figure 22, where relative values of elongation components are plotted against load values. Figure 22A represents the original behavior as obtained in a single extension of the thread. Figure 22B demonstrates the elongation components (correlated to the original fiber length) plotted against the initial and ultimate load values to which the thread was stretched. Two curves are shown, therefore, for each elongation component, although they do not differ markedly from each other. Increased permanent set and reduced delayed recovery without significant alteration of the immediate elastic recovery appear after cycling when compared to the behavior in a single extension.

The comparatively high permanent set obtained during the cycling operation, of course, also markedly alters the recovery, making the thread more elastic. This is apparent from the recovery behavior of the thread after mechanical conditioning to the strain level of 5% (in 20 cycles and after 1 hr. relaxation) shown by four curves (Figure 21B *) and by a rectangular graph (Figure 22C). In both demonstrations markedly reduced permanent set appears if compared with the original behavior (Figures 21A and 22A). At the breaking point almost unaltered actual values of immediate and delayed recovery are shown after mechanical conditioning, while higher relative values of these components appear than originally since they are correlated to reduced elongations.

The demonstration of the recovery behavior by four curves (Figure 21) permits the separation of work components: the immediately recoverable work, the creeping recoverable work, and the unrecoverable work, as shown in Figure 26. The sum of these components is the total work necessary for rupture (10.6 g.-cm./gx. before and 8.2 g.-cm./gx. after mechanical conditioning for 1 m. fiber length), which is represented by the area under the stress-strain curve.

The immediately and creeping recoverable work reflect that part of the total work absorption which is regained spontaneously after the tension is released. They appear almost unaffected if the extension is repeated in each cycle. Immediately recoverable work has to be considered in evaluating frequently repeated deformations (in dynamic fatigue tests, in flex abrasion if performed at high speed, in the sewing operation). Both recoverable work components must be taken into account for tensile deformations if frequently repeated and separated from each other by rest periods, as it generally oc-

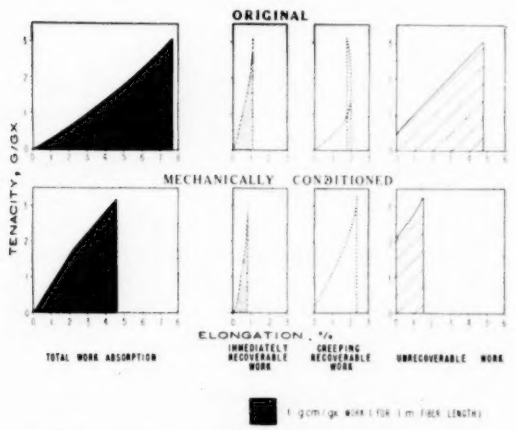


FIG. 26. *Work components of 56/3 cotton thread.*

* Tenacity in Figure 21B is correlated to the decreased grex (280), and elongation to the new fiber length (after mechanical conditioning). This presentation is thus identical to that of curve *IV* in Figure 5A.

TABLE IX. WORK COMPONENTS OF 56/3 COTTON THREAD

	Original	Mechanically conditioned
Actual values (g.-cm./gx.) (for 1 m. fiber length)		
Immediately recoverable	1.1	0.7
Creeping recoverable	1.1	3.5
Unrecoverable	8.4	4.0
Total	10.6	8.2
Relative values (% of total work)		
Immediately recoverable	10	9
Creeping recoverable	11	43
Unrecoverable	79	48

curs in service and in wear tests. The unrecoverable work component is significant for the first deformation process and it disappears after the first extension, increasing the fiber length and diminishing the cross section. Its disappearance is manifested by the difference in the areas of the first and subsequent cycles, as it is observable for acetate and Vinyon NORU in Figure 9 and for the cotton thread in Figure 23. An excessive unrecoverable work component is the origin of poor dimensional stability and poor wrinkle-resistance, and it affects indirectly many other functional properties of textiles (hand, comfort, durability). A high unrecoverable work component in textile fibers is generally disadvantageous, although to some extent it can be desirable or even necessary for special end-uses (*e.g.*, in sewing threads).

Numerical data of actual and relative values of the work components of the cotton thread are listed in Table IX (original values and values obtained after mechanical conditioning to a 5% elongation level). The same values are also shown graphically in Figure 27. They reveal that the immediately recoverable work does not change appreciably, while that which recovers creeping increases, indicating that mechanical conditioning does not consist merely in the elimination of unrecoverable work. Total work of rupture decreases after mechanical conditioning; this is primarily the result of a diminished unrecoverable work component, suggesting again that unrecoverable work is of comparatively little value. It must be noted that during the mechanical conditioning procedure performed only 23% of the total work absorption was lost. This reduction is rather small in view of the high conditioning level of 5% elongation, which is equivalent to 65% of the extensibility, 55% of the breaking tenacity, and 40% of the total energy of rupture. The comparatively small loss in energy can be understood, however, since only the unrecoverable work decreased markedly.

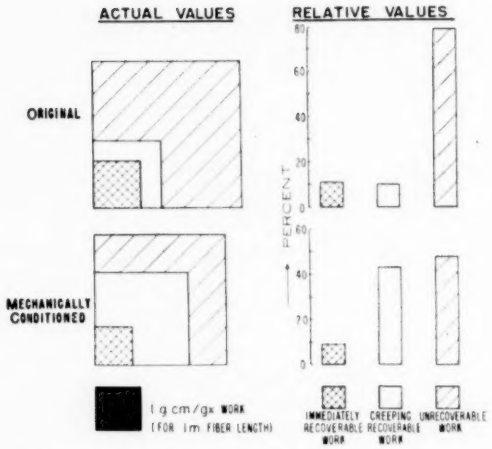


FIG. 27. *Work components of 56/3 cotton thread.*

Summary

The response of various textile fibers to stretching varies widely according to their inherent properties as manifested in their delayed recovery and permanent set (plastic flow).

If mechanical conditioning occurs, the new extensibility is less than the original without much affecting the over-all extensibility of the fiber, except in the case of notable slippage. Mechanical conditioning can cause stress hardening as well as fatigue, and it is always connected with loss in work necessary to rupture. It reduces the unrecoverable part of the elongation and it increases the ratio of immediate and delayed elastic recovery to the total elongation, making the fibers more elastic. Mechanical conditioning also affects the characteristic shape of the stress-strain relationship. The yield point may become either less or more pronounced by mechanical conditioning; it can increase or decrease; even additional new yield points can appear. The initial modulus can remain unchanged; it may increase or decrease. The new properties of fibers due to a previous strain are partly temporary and partly permanent. They disappear to some extent spontaneously and to a greater degree when treated by heat or a swelling agent.

A knowledge of the degree to which the properties of a fiber are affected by stress or strain is necessary for the understanding of its behavior. It is useful for the control of processes in which textile materials are subjected to stress and strain either intentionally or unintentionally. The alteration of fiber properties due to stretching also indicates whether or not a textile material has functional stability in service.

Acknowledgments

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Relationship Between Various Surface Properties of Wool Fibers

Part III: Sorption of Dyes and Acids in Wool Fibers *

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Abstract

Wool fibers were treated with alcoholic potash for different periods of time. The diffusion rate of dyes and acids into wool fibers was measured. It was found that the epicuticle largely controls the diffusion rate. The differences in permeability of the epicuticle in different parts of the fiber complicate a mathematical treatment of the diffusion data. A theory is given in which the differences in permeability of the epicuticle are thought to be dependent on the polarity of the surface layer.

Introduction

The diffusion of matter in a solid like a wool fiber is not by definition a surface property. The rate of diffusion, however, may be partly controlled by the conditions at the interface between the fiber and the surrounding medium. One is therefore justified to include diffusion with the surface properties of wool fibers. It has been shown by several authors that the rate of sorption of many dyes is controlled by the cuticle of the fiber, the most extensive investigation being that of Millson and Turl [15]. For the sorption of hydrochloric acid, it was shown by Lindberg [11] that the rate-controlling part of the cuticle is the epicuticle. If this is also true for sorption and desorption phenomena involving ions, the state of the epicuticle must have an important bearing on textile processses like dyeing, carbonizing, rinsing, and so on.

The well-known phenomenon of tippy dyeing, for instance, was shown by Watkins *et al.* [24] to disappear completely after treatment of the fibers with alcoholic potash. Under appropriate conditions the action of this reagent is limited to the epicuticle, which was shown in Parts I [12] and II [13] of this series. It is thus important to get conclusive evidence for the role of the epicuticle in sorption processes so that steps can be taken to modify either the surface of the fiber or the processes in order to avoid the complications introduced by fibers, which are very heterogeneous with regard to the diffusion rate. The present paper deals with the sorption of dyes and acids under controlled conditions, using the experimental material described in Part I.

Sorption of Dyes

The rate of sorption of dyes onto fibers is generally determined colorimetrically by measuring the concentration of dye in the dye bath after different dyeing times. The following experimental conditions were used here. A 1-liter beaker was equipped with a screw stirrer and a cover to prevent liquor losses by evaporation. A volume of 850 ml. of the dye liquor was heated in the beaker to the dyeing temperature, and the temperature was then controlled by means of a thermostat. Fibers were cut into pieces of about 2 mm. length. This was done in order to obtain better stirring and to eliminate concentration gradients in the liquid [11, 17]. Samples of 2 g. were wetted out with a blank dye bath in a glass tube and plunged into the bath. The stirrer was operated at a rate of about 1,000 r.p.m. Aliquots of 10 ml. were taken from the dye bath at intervals of 2 min. up to 12 min. Then the dyeing was continued to equilibrium. The concentration of dye in the dye bath was determined by means of a Lumetron colorimeter.

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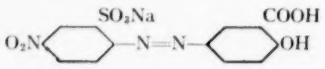
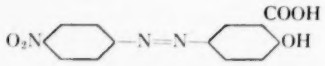
† Director of Research.

The dyes used in the experiments were Eriochrome Phosphine R (Geigy) (Colour Index No. 157)



and Solochrome Orange MS (I.C.I.) (Colour Index No. 40)



The dyes were commercial preparations, and no attempt was made to purify them. The concentration of dye in the dye bath was 0.1 g./l. for both dyes, and the bath was buffered by an acetate buffer to pH 4.5 for the first dye and pH 3.5 for the second dye. The first dye was monosulfonated and the second dye was nonsulfonated. These two dyes were previously investigated by Barritt and Elsworth [1], who related dye constitution to dyeing properties using normal and chlorinated wool.

The following samples were selected from the different pretreatments described in Part I: ether-extracted, ether- and alcohol-extracted, and alcoholic potash (4 min.).

The amount of dye on the fiber at the time t is M_t, which is equal to $V(c_o - c_t)$, where c_t is the concentration of dye in the bath at the time t and V is the volume of the bath. Dyeings were made at three different temperatures. The results are given in Figures 1–6. Each curve is the mean of two dyeings.

It is seen from Figures 1–3 that for all temperatures the rate of sorption of the monosulfonated dye was much greater for the sample treated in alcoholic potash for 4 min. than for the sample extracted with ether. The ether- and alcohol-extracted sample was intermediate between these two. For the nonsulfonated dye the same result was obtained, although the differences here were much smaller.

Freney and Lipson [5] and Kienle *et al.* [9] found previously that treatment with alcoholic potash greatly increases the rate of dyeing, and thus far the present results do not give any new contribution to our knowledge. However, precautions were taken here to make sure that the treatment was confined to the surface layer of the fiber. The fact that the same result nevertheless was obtained shows that the epicuticle largely controls the rate of dye sorption. The position of the prime diffusion barrier in the cuticle suggested by several authors [2, 7, 20] is thus narrowed down to the epicuticle.

TABLE I. FRACTION OF DYE IN THE BATH AFTER EQUILIBRIUM IS REACHED (c_∞/c_o)

Eriochrome Phosphine R			
Treatment	60°C	65°C	70°C
Ether-extracted	.24	.27	.29
Ether- and alcohol-extracted	.23	.26	.28
Alcoholic potash (4 min.)	.22	.24	.28

Solochrome Orange MS			
Treatment	40°C	45°C	50°C
Ether-extracted	.19	.22	.25
Ether- and alcohol-extracted	.18	.21	.24
Alcoholic potash (4 min.)	.18	.21	.24

Townend and Simpson [23] showed that dry chlorinated wool dyes more rapidly than normal wool. This difference is more pronounced if the degree of sulfonation of the dye is increased. They used three dyes, which differed only in the degree of sulfonation. Their results are similar to those obtained by Barritt and Elsworth [1] and to those presented here. If the difference in dyeing behavior between these samples, which differ only with regard to the epicuticle, is dependent on the basicity of the dye, then it might be assumed that the barrier formed by the epicuticle is electrical in nature. This point will be discussed further in connection with the acid sorption.

The equilibrium values, c_∞/c_o, for the different treatments (Table I) were practically the same.

Distribution of Dye on the Fiber

Measurements of dyeing rates by methods described above give only the mean values of the dyeing rates of different fibers or different parts of the fibers. No information on the distribution of the rate for different fibers or parts of fibers is obtained by this procedure. If, however, the dyeing is interrupted at an early stage, the distribution of the dye over the fiber may give an indication of the distribution of the dyeing rates. As pointed out in Part I [12], most staining agents behave like ordinary dyes, and therefore these agents measure the distribution of the dyeing rate over different parts of the fibers. Millson and Turl [16] successfully used the microdyeoscope to study the initial distribution of dyes over the fiber. They found that all acid and milling wool dyes were unevenly distributed over a normal fiber in the first stage of the dyeing, and attributed this to differences in permeability of the cuticle. This distribution can also be expressed quantitatively. If the fiber parts are divided in different classes according to the depth

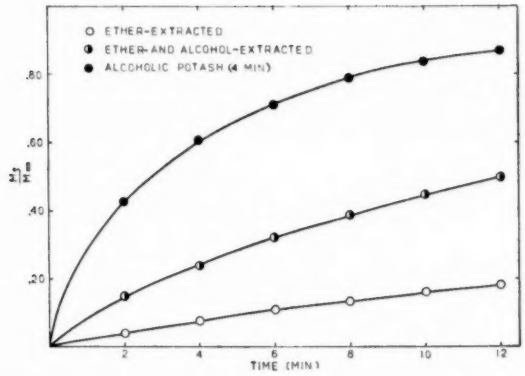


FIG 1. *Dyeing curves for Eriochrome Phosphine R. Dyeing temperature, 60°C.*

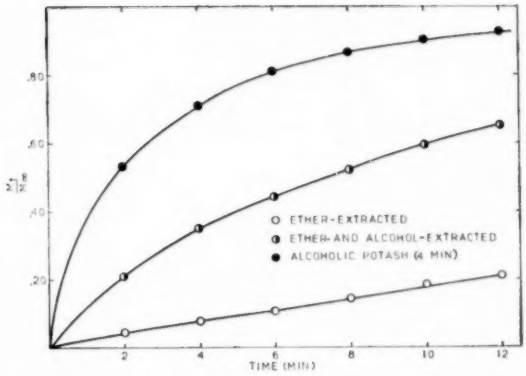


FIG 2. *Dyeing curves for Eriochrome Phosphine R. Dyeing temperature, 65°C.*

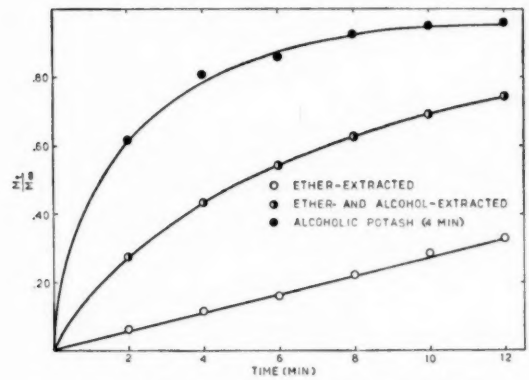


FIG 3. *Dyeing curves for Eriochrome Phosphine R. Dyeing temperature, 70°C.*

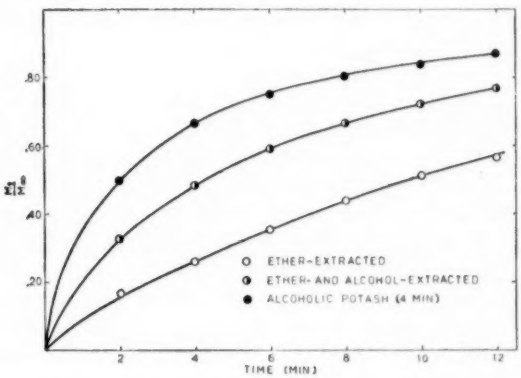


FIG. 4. *Dyeing curves for Solochrome Orange MS. Dyeing temperature, 40°C.*

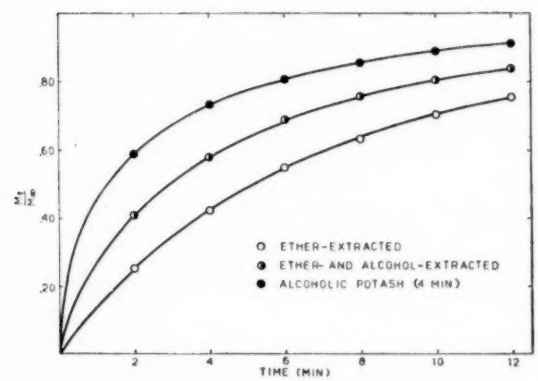


FIG. 5. *Dyeing curves for Solochrome Orange MS. Dyeing temperature, 45°C.*

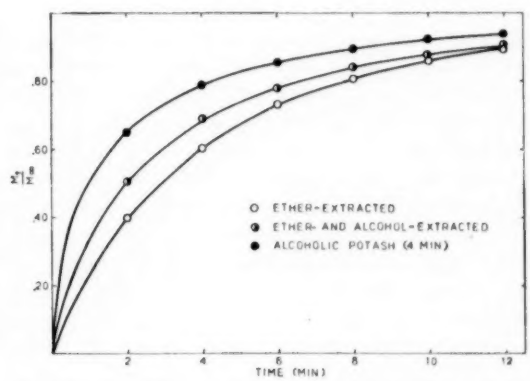


FIG. 6. *Dyeing curves for Solochrome Orange MS. Dyeing temperature, 50°C.*

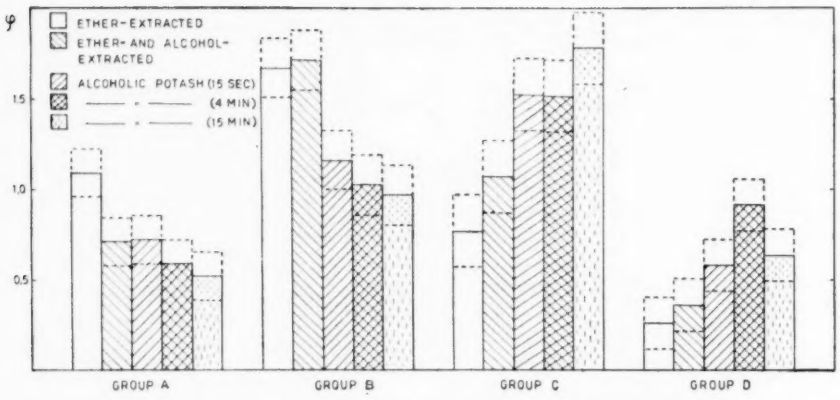


FIG. 7. *Values of φ for different groups and different treatments.*

of the color [12], a distribution curve is obtained. Differences between distribution curves can be evaluated by means of statistical methods [21].

Different samples of wool fibers were stained with Naphthalene Scarlet 4 R 120 in the following way: The fibers were ground in a Wiley mill,* and a small amount was put into a dye bath containing 25 ml. of a 0.01% dye solution buffered to pH 3.5. The temperature was 40°C. After 10 min. the fibers were filtered off and washed. After drying, the fiber samples were mixed thoroughly. The mixing was necessary because different fibers having different wetting properties were separated by flotation on the filter paper. The fibers were mounted on microscope slides and examined. One-hundred fibers from each sample were counted and divided into four classes: (*a*) unstained, (*b*) stained in spots (less than 50% of the surface), (*c*) slightly stained, and (*d*) heavily stained.

The fiber ends were always heavily stained, but these stains were disregarded. Two slides from each sample were examined by five different observers. The mean values of these 10 determinations are given in Table II.

If P is the population frequency of any class, the theoretical variance is $P(1-P)/n$, where n is the total number of fibers counted ($n = 100$). To make this variance independent of the mean, a transformation of the data is necessary. The proper transformation to use in this case is the inverse sine transformation [22]. The variance of the transformed data is then equal to $1/n$. An analysis of variance can then be carried out using these transformed data. The analysis of variance for group *c* is given in Table IV. Table III gives the values of p (p is the estimate of the population value P) together with values of $\varphi = 2 \arcsin \sqrt{p}$.

The theoretical value of the error is $1/n = 0.01$. The actual value is not far from the theoretical one, which means that the different observers could obtain reproducible values in two consecutive measurements. Similar results were obtained also for other groups.

The difference between different observers is not significant if it is compared to the interaction. For other groups, however, there were significant differences between observers, which might be expected because it is difficult to agree on group boundaries. The significant interaction between observers and treatments means that the observers could not reproduce their measurements after long periods, or that their judgments were influenced by the general character of the sample—*e.g.*, if there were many unstained fibers or not. In order to derive fiducial limits for the different treatment means (summed over different observers), the interaction must be used as error. In Figure 7 the means of φ for different groups and different treatments are given as

TABLE II. NUMBER OF FIBERS IN DIFFERENT GROUPS

Treatment	*a*	*b*	*c*	*d*
Ether-extracted	27.9	54.4	15.6	2.1
Ether- and alcohol-extracted	12.9	56.5	26.8	3.8
Alcoholic potash (15 sec.)	13.1	30.0	47.5	9.4
Alcoholic potash (4 min.)	8.8	24.6	46.9	19.7
Alcoholic potash (15 min.)	7.1	22.1	60.5	10.3

* The Wiley mill has two knives and a rotating cutter.

TABLE III. VALUES OF p AND φ

Treatment	Observer 1 p	1 φ	2 p	2 φ	3 p	3 φ	4 p	4 φ	5 p	5 φ	Mean values of φ
Ether-extracted	.13	.74	.17	.85	.31	1.18	.06	.49	.13	.74	
	.13	.74	.14	.77	.34	1.25			.15	.80	0.76
Ether- and alcohol-extracted	.28	1.12	.21	.95	.44	1.45	.27	1.09	.13	.74	
	.22	.98	.28	1.12	.49	1.55	.27	1.09	.09	.61	1.07
Alcoholic potash (15 sec.)	.46	1.49	.41	1.39	.44	1.45	.41	1.39	.46	1.49	
	.50	1.57	.39	1.35	.61	1.79	.58	1.73	.49	1.55	1.52
Alcoholic potash (4 min.)	.50	1.57	.38	1.33	.50	1.57	.34	1.25	.64	1.85	
	.52	1.61	.52	1.61	.46	1.49	.28	1.12	.55	1.67	1.51
Alcoholic potash (15 min.)	.60	1.77	.62	1.81	.63	1.83	.63	1.83	.56	1.69	
	.58	1.73	.56	1.69	.65	1.88	.61	1.79	.61	1.79	1.78
Mean values of φ		1.33		1.29		1.54		1.18		1.29	

a chimney diagram. The dotted lines are the 0.95 fiducial limits. From Figure 7 and Table II it is seen that there is a tendency towards more heavily stained fibers with increasing severity of treatment.

It seems likely that the increase in over-all dyeing rate with time of treatment was due mainly to an increase in dyeing rates of those fibers which previously had low dyeing rates, while those fibers which were heavily stained were unaffected by the treatment. The result was smaller differences in dyeing rates between different parts of a fiber or a larger relative area available for dye penetration. The whole question of the sorption rate of a fiber is obviously complicated by the fact that the rate of diffusion across the phase boundary is different in different parts of a fiber. This fact must be considered when attempts are made to explain the behavior of wool fibers in terms of theoretical diffusion equations.

Sorption of Acids

A wool fiber can be regarded as being approximately a cylinder of infinite length. For a solute diffusing from a bath into this cylinder, Fick's second law is

$$\frac{\delta c}{\delta t} = \frac{D}{r}\frac{\delta}{\delta r}\left(r\frac{\delta c}{\delta r}\right), \qquad (1)$$

where c is the concentration of the solute, t is the time, r is the radius of the cylinder, and D is the diffusion coefficient. The value of D is here assumed to be independent of the concentration, c.

This differential equation is valid only for homogeneous cylinders. From the preceding section dealing with the distribution of dye over the fiber it can, however, be concluded that a wool fiber is not homogeneous as regards diffusion of dyes into the fiber. It might be safe to assume that the same is true for hydrochloric acid. It is also evident from dyeing experiments that the main cause of the change of diffusion rates along the fiber must be sought in the surface layer. It has even been suggested [11, 14] that the rate of diffusion across the surface layer varies from zero to that in the bulk of the fiber.

It is then obvious that a considerable amount of axial diffusion will take part within the fiber together with the radial diffusion. This will complicate a mathematical solution of the problem so as to make it prohibitive, since the distribution along the fiber of the diffusion rates across the surface layer must be known, and there is no reason to assume that axial and radial diffusion coefficients have the same values in an anisotropic substance like a wool fiber. Lindberg [11] showed, however, that a solution of equation (1), in spite of the approximations involved, will give a good description of experimental data on the rate of sorption of hydrochloric acid. In order to solve equation (1) formally, a further approximation must be made. In the case of hydro-

TABLE IV. ANALYSIS OF VARIANCE OF φ

Source of variation	Degrees of freedom	Sum of squares	Mean squares†
Total	49	9.1255	
Between observers	4	.7207	.1802
Between treatments	4	6.6786	1.6697***
Interaction: observers × treatments	16	1.3567	.0848***
Error	25	.3695	.0148

† In this and subsequent tables the asterisks *, **, and *** are used to indicate statistical significance at the 95%, 99%, and 99.9% levels, respectively.

chloric, we have diffusion combined with sorption on active sites in the fiber. The sorption isotherm for hydrochloric acid given by Gilbert and Rideal [6] can be written

$$\frac{s}{s_{max} - s} = R'c, \qquad (2)$$

where s is the acid-binding capacity of the wool fiber at the concentration c in the bath, and R' is the partition coefficient.

Over a short range of concentration, equation (2) can be substituted by $s = Rc$, which will greatly simplify the solution of the differential equation. By assuming that the diffusion process is rate-determining, equation (1) was solved by Wilson [25] as follows:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{n=\infty} \frac{4\alpha(1+\alpha)}{4 + 4\alpha + \alpha^2 q_n^2} e^{-q_n^2 \beta t}, \qquad (3)$$

where M_t is the amount of solute in the fiber at time t, and q_n is a non-zero, positive root of the equation

$$\alpha q_n J_o(q_n) + 2J_1(q_n) = 0, \qquad (4)$$

where $J_o(q_n)$ and $J_1(q_n)$ are Bessel functions of zero and first order, respectively.

$$\beta = \frac{D}{(R+1)a^2} \qquad (5)$$

and

$$\alpha = \frac{A}{\pi a^2 (R+1)} = \frac{B_\infty}{M_\infty}, \qquad (6)$$

where A is the volume of the bath per unit length of the fiber, B_t is the amount of solute in the bath at time t, and a is the radius of the fiber.

For small values of βt, the series in equation (6) converges slowly. To avoid this difficulty, two alternative solutions were derived by Crank [4]:

$$\frac{M_t}{M_\infty} = \frac{2}{\alpha}(1+\alpha)\left[\frac{2}{\sqrt{\pi}}\sqrt{\beta t} - \left(\frac{1}{2} + \frac{2}{\alpha}\right)\beta t - \frac{4}{3\sqrt{\pi}}\left(\frac{1}{8} - \frac{2}{\alpha} - \frac{4}{\alpha^2}\right)(\sqrt{\beta t})^3 \cdots\right]; \qquad (7)$$

and for small α and small βt,

$$\frac{M_t}{M_\infty} = \frac{1+\alpha}{1+\frac{1}{4}\alpha}\left[1 - e^{4(1+\frac{1}{4}\alpha)^2 \frac{\beta t}{\alpha^2}} \times \operatorname{erfc}\left(2(1+\tfrac{1}{4}\alpha)\frac{\sqrt{\beta t}}{\alpha}\right)\right], \qquad (8)$$

where

$$\operatorname{erfc} x = 1 - \frac{2}{\sqrt{\pi}}\int_o^x e^{-z^2}\, dz.$$

Values for M_t/M_x are given in Table V for different values of α and βt.

TABLE V. VALUES OF M_t/M_∞ FOR VARIOUS VALUES OF βt AND α

	$\frac{M_\infty}{M_\infty + B_\infty}$				
$\beta t \cdot 10^3$	.45	.35	.25	.15	.05
2	.169	.146	.129	.115	.104
3	.203	.177	.156	.140	.126
4	.232	.202	.178	.160	.145
5	.255	.223	.198	.178	.162
6	.276	.242	.215	.194	.176
8	.313	.275	.246	.222	.202
10	.343	.304	.272	.246	.225
12	.370	.328	.295	.268	.245
15	.404	.360	.325	.296	.272
18	.434	.389	.353	.322	.296
21	.461	.415	.376	.345	.318
24	.484	.437	.398	.365	.337
28	.513	.465	.425	.391	.355
32	.538	.490	.449	.414	.384
36	.561	.512	.471	.435	.405
40	.582	.533	.491	.455	.424
46	.610	.561	.519	.482	.451
55	.646	.598	.556	.519	.486
65	.681	.634	.592	.555	.522
75	.711	.665	.624	.587	.554
85	.737	.693	.653	.616	.583
95	.760	.717	.678	.642	.609
110	.791	.750	.712	.677	.644
130	.824	.787	.751	.718	.686
150	.852	.818	.785	.753	.723
170	.875	.844	.813	.783	.754
200	.903	.876	.849	.822	.795

Values of D obtained in this way are, of course, only apparent diffusion coefficients. The value of D is dependent on D_e, the diffusion coefficient in the surface layer, on D_a, the axial diffusion coefficient, and on D_r, the radial diffusion coefficient. The apparent value can be changed by changing D_a or D_r or by changing the average value of D_e. It is important to note this fact, when sorption rates of dyes or acids are used in order to draw conclusions regarding structural changes of the fibers.

The reason why equation (1) can be used to describe the experimental data might perhaps be found in the fact that the general shapes of the radial and axial diffusion curves are similar. This can be seen from Figure 8. The time axis was adjusted so that the two curves would intersect each other.

Experimental

The experimental technique used to determine the rate of sorption of acids was the same as that described by Lindberg [11]. The fibers were cut in short pieces by a cutting device in order to get a more uniform suspension in a moderately well stirred bath.

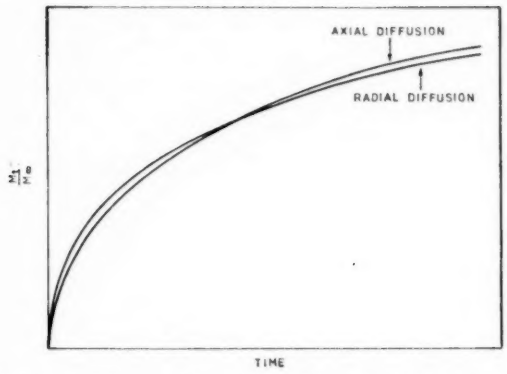


FIG. 8. *Diffusion curves for axial and radial diffusion.*

A sample weighing about 0.5 g. was thoroughly wetted out with 5 ml. of distilled water in a small glass tube with a stopper in one end. A beaker containing 250 ml. of dilute hydrochloric acid was placed in a thermostat and equipped with a stirrer and a conductivity cell. The cell had two parallel electrode plates, which were uncovered so that the fiber suspension could pass through the cell when the bath was agitated. A reference cell was placed in an acid solution in the thermostat bath.

The change of the conductivity of the solution due to the sorption of acid onto the fibers was recorded automatically by means of a Micromax conductivity bridge. It is a Wheatstone bridge which is automatically balanced 25 times per min. by moving a contact over a slide-wire. The position of the contact is shown on the recording paper and gives the ratio of the conductivity of the bath to the conductivity of the reference solution.

While the stirrer was going, the stopper was removed from the glass tube and the fibers were plunged into the acid solution. The short fibers were immediately dispersed in the bath and did not interfere with the conductivity measurements. The sorption of the acid could be followed from the decrease in the conductivity ratio. The concentration of hydrochloric acid in the bath could be calculated from this ratio. In Figure 9 an actual curve is reproduced. The experiment was continued until equilibrium was established, which gave M_∞ and B_∞. At any time t the value of M_t could be determined and also the ratio M_t/M_∞. By interpolating in Table V, values of βt could be obtained for different values of M_t/M_∞ and the value of α in question. The value of D was then calculated from equation (6), which can be rewritten

$$D = \frac{\beta V \rho a^2 M_\infty}{g B_\infty}, \qquad (9)$$

where V is the volume of the bath, ρ is the specific gravity of the fiber, and g is the weight of the fiber sample.

In order to determine the influence of stirring rate, liquor ratio, and length of fiber on the results, a preliminary experiment was run varying these variables. It was desired to investigate four stirring rates: 1,000, 2,000, 2,500, and 3,000 r.p.m. (The stirrer was a bent glass rod.) At 1,000 r.p.m. the fibres were just held in suspension, and over 3,000 r.p.m. the bath was splashed out of the beaker. The fibers were cut to 4, 3, 2, and 1 mm. lengths. The values of the fiber lengths are approximate averages. The amounts of wool used in 255 ml. of 0.005N HCl were 0.7, 0.6, 0.5, and 0.4 g. The temperature was 25°C. The experiments were planned as a 4×4 Latin Square. The wool used was of unknown origin. The experimental conditions and the results are given in Table VI.

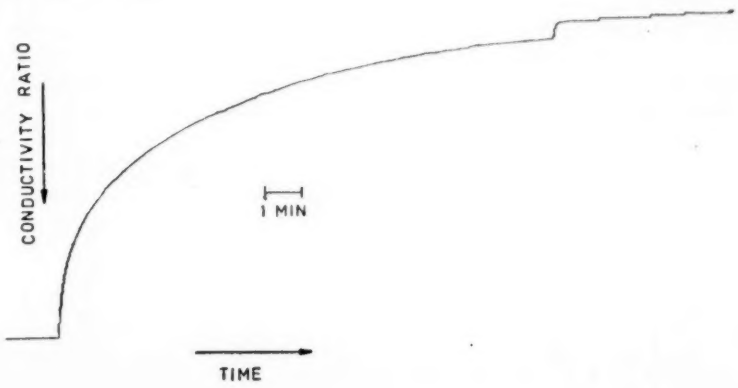


FIG. 9. *Actual diffusion curve for hydrochloric acid from the Micromax recorder.*

TABLE VI. VALUES OF $D \cdot 10^6$ CM.²/MIN. FOR DIFFERENT EXPERIMENTAL CONDITIONS (THE FIBER LENGTH (MM.) IS GIVEN BELOW EACH FIGURE)

Rate of stirring (r.p.m.)	Weight of sample: 0.4 g.	0.5 g.	0.6 g.	0.7 g.	Mean values
1,000	.790	.891	.864	.953	.875
	1	2	3	4	
2,000	.981	.897	.906	.940	.931
	2	1	4	3	
2,500	.964	.785	.904	.980	.908
	4	3	2	1	
3,000	1.153	.852	.936	.879	.955
	3	4	1	2	
Mean values	.972	.856	.903	.938	
	1	2	3	4	
Mean values for fiber length	.901	.914	.936	.919	

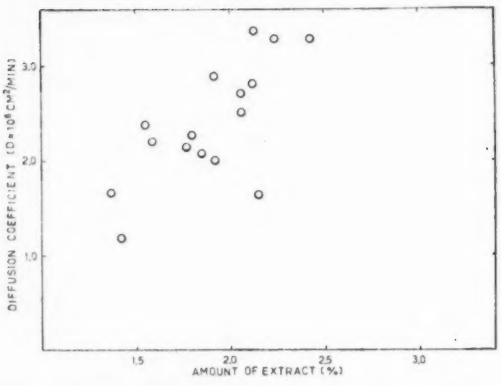


FIG. 10. *Relation between the diffusion coefficient and the amount of fatty matters extracted from the fibers.*

An analysis of variance showed that none of the factors which were varied during the experiment had any influence on the results greater than the experimental error. The coefficient of variation was 9.4%. The stirring rate is especially interesting; stirring is not critical when chopped fibers are used, provided that the stirring rate is sufficient to keep the fibers in uniform suspension. The liquor ratio had no influence on the value of D, which means that the weight of the sample can vary. The weight must be known, however, in order to calculate D from equation (9). Some criticism can be raised against cutting the fibers in short pieces. The formation of new end surfaces might increase the total surface area and thus influence the results. From the present experiments it was evident that the relative increase in surface area was negligible. Finally, the fibers were cut in a Wiley mill to get a still better suspension, and even then there was no increase in D compared to the results obtained when using longer fibers.

The next step was to investigate the effect of the extractions of the fibers. Untreated fibers were divided into 16 lots with 2 g. in each lot. These were extracted in 1, 2, 3, and 4 steps in the same manner as described in Part I [12] using diethyl ether at a temperature of 20°C, ethyl alcohol at 20°C, ethyl alcohol at 50°C, and a combined extraction of diethyl ether at 20°C and ethyl alcohol at 50°. In the latter case the samples were first extracted in 1–4 steps with diethyl ether and then in 1–4 steps with alcohol. The amount of fatty matters extracted in each step was determined by evaporating the solvent and weighing the residue. The residues, e, are given in Table VII as percent of the extracted sample weight.

The values of D were determined for each of the 16 samples. Two tests were run on each sample. The fibers were cut to an approximate length of 2 mm., the sample weight used was 0.5 g., and the temperature was 25°C. Mean values of D are given in Table VII. Figure 10 gives the relation between D and amount of extract.

It is evident that there is a relation between the diffusion coefficient and the amount of fatty material extracted from the fiber. The most likely explanation of this is that the fatty matter forms a layer on the damaged surface of the fiber and thereby reduces

TABLE VII. AMOUNT OF FATTY MATTERS EXTRACTED AND VALUES OF $D \cdot 10^6$ CM.²/MIN.

Extraction	Number of step 1		2		3		4	
	e	D	e	D	e	D	e	D
Diethyl ether, 20°C	1.42	1.19	1.79	2.26	1.59	2.20	1.85	2.07
Ethyl alcohol, 20°C	1.37	1.65	1.76	2.13	1.92	2.00	2.15	1.65
Ethyl alcohol, 50°C	1.55	2.39	2.05	2.70	2.14	2.80	2.24	3.27
Ethyl alcohol, 50°C, and diethyl ether, 20°C	1.92	2.89	2.06	2.49	2.13	3.36	2.43	3.27

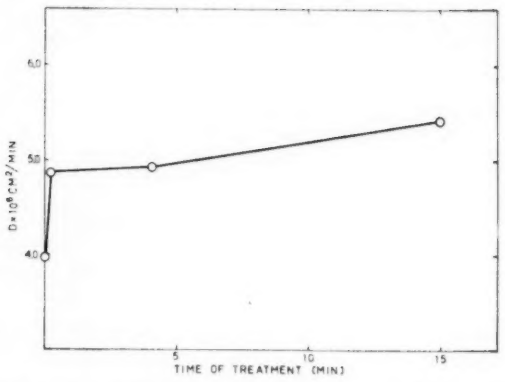


FIG. 11. *Relation between the diffusion coefficient and the time of treatment with alcoholic potash.*

the surface available for penetration of the acid. Some soaplike ions might also be sorbed on sites where normally the acid is sorbed, thus slowing down the diffusion.

Four of the samples pretreated according to Part I—namely, ether- and alcohol-extracted, and alcoholic potash treated for 15 sec., 4 min., and 15 min., respectively, were then investigated. The values of D were determined for these samples at two concentrations of HCl, 0.005N and 0.001N, and at four temperatures, 20°, 24.9°, 29.9°, and 35°C. The fibers were cut in a Wiley mill, and the sample weight used was 0.5 g. Other experimental conditions were the same as in the preceding experiments. The results are given in Table VIII. It is seen that the mean value of D for 0.001N HCl was slightly higher than that for 0.005N HCl. The diffusion coefficient increased with the time of treatment. This increase, however, was not so great as the corresponding increase in the rate of dye sorption. From Figures 1–3 is seen that the ratio of the half-dyeing times for ether- and alcohol-extracted and alcoholic potash-treated (4 min.) fibers was about 4. The corresponding ratio for the diffusion coefficients in Table VIII was 1.25. In Figure 11 the mean values of D are plotted against time of treatment in alcoholic potash. The same sharp increase in the diffusion rate was obtained during the first few seconds of treatment, as previously reported by Lindberg [11]. This shows conclusively that the surface layer of the fiber largely controls the rate of diffusion and that the epicuticle is very sensitive to alkali used in alcoholic solutions.

Like most other chemical reactions the rate of diffusion increases with increase in temperature. The change of reaction rate with temperature proved to be of great value in the study of reaction mechanisms. The theory of absolute reaction rates proposed mainly by Eyring and coworkers (see [8]) can be employed also to problems of diffusion. The relation between D and T is of the following form:

$$\ln \frac{D}{T} = \ln d^2 + \ln \frac{k}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}, \qquad (10)$$

where T is the absolute temperature, d is the distance between two equilibrium positions of the diffusing ion, k is Boltzmann's constant, h is Planck's constant,

TABLE VIII. VALUES OF $D \cdot 10^6$ CM.²/MIN.

Normality of HCl	Treatment	20.0°C	24.9°C	29.9°C	35.0°C
0.005	1. Ether- and alcohol-extracted	2.48	3.35	4.32	5.10
	2. Alcoholic potash (15 sec.)	3.08	4.00	5.57	6.11
	3. Alcoholic potash (4 min.)	3.48	4.36	4.98	6.17
	4. Alcoholic potash (15 min.)	3.98	4.70	5.56	6.78
0.001	1. Ether- and alcohol-extracted	2.70	3.45	4.57	5.87
	2. Alcoholic potash (15 sec.)	3.48	4.34	5.54	6.83
	3. Alcoholic potash (4 min.)	3.60	4.57	5.54	6.77
	4. Alcoholic potash (15 min.)	4.11	5.05	5.85	7.35

Mean values

Treatments	1	2	3	4
	3.98	4.87	4.93	5.42
Temperatures	20.0°C	24.9°C	29.9°C	35.0°C
	3.36	4.23	5.24	6.37
Concentrations	0.005	0.001		
	4.63	4.98		

TABLE IX. VALUES OF LOG $\frac{D}{T} \cdot 10^9$

Normality of HCl	Treatment	$\frac{1}{T} \cdot 10^3$ 3.410	3.355	3.300	3.245
0.005	Ether- and alcohol-extracted	.927	1.041	1.154	1.219
	Alcoholic potash (15 sec.)	1.021	1.128	1.264	1.297
	Alcoholic potash (4 min.)	1.075	1.165	1.216	1.320
	Alcoholic potash (15 min.)	1.133	1.198	1.264	1.342
0.001	Ether- and alcohol-extracted	.964	1.063	1.178	1.280
	Alcoholic potash (15 sec.)	1.075	1.163	1.262	1.346
	Alcoholic potash (4 min.)	1.089	1.186	1.262	1.342
	Alcoholic potash (15 min.)	1.147	1.229	1.286	1.378

TABLE X. ANALYSIS OF VARIANCE

Source of variation	Degrees of freedom	Sum of squares	Mean squares
Total	31	.406938	
Between concentrations	1	.007938	.007938***
Between temperatures			
Linear component	1	.300849	.300849***
Quadratic component	1	.000465	.000465
Cubic component	1	.000026	.000026
Between treatments	3	.087960	.029320***
Interactions			
Concentration × treatment	3	.000122	.000041
Concentration × temperature	3	.000652	.000217
Temperature × treatment			
Linear component	3	.005846	.001949**
Quadratic component	3	.000681	.000227
Cubic component	3	.001118	.000373
Error	9	.001281	.000142

ΔS^* is the entropy of activation, ΔH^* is the heat of activation, and $\boldsymbol{R}$ is the gas constant. From the data in Table VIII it is possible to determine ΔS^* and ΔH^* provided d is known. The value of d can be estimated from the maximum number of active sites available for acid sorption:

$$d = \sqrt[3]{\frac{1+v}{\rho s_{\max} N}}, \qquad (11)$$

where v is the fraction of volume swelling in water, ρ is the specific gravity for dry wool, $s_{\max}$ is the number of moles per gram of wool, and N is Avogadro's number. For $v = 0.30$, $\rho = 1.30$, and $s_{\max} = 0.8 \cdot 10^{-3}$, the value of d is 5.9 Å. In Table IX the values of log (D/T) are given. An analysis of variance was carried out on these data, and is shown in Table X.

From Table X it is seen that the difference between the values of D for different concentrations given in Table VIII was significant. It is also obvious that if log (D/T) is plotted against $1/T$, there is no significant deviation from a straight line, which indicates that equation (10) is valid.

The most interesting result revealed by the analysis was the significant interaction of the linear component between temperature and treatment. This means that ΔH^* was different for different treatments. The values for ΔH^* and ΔS^* were calculated and are given in Table XI. There was no difference in ΔH^* or ΔS^* for different concentrations, and therefore the means for the two concentrations are given.

Reese and Eyring [19] studied the diffusion of NaOH and Na_2S in human hair, and the results given by them for D, ΔH^*, and ΔS^* are of the same order of magnitude as those given here for HCl. A change in the heat of activation for a reaction is generally interpreted as a change in the reaction mechanism, in this case a change in the diffusion mechanism in the surface layer. But D is some function of D_e, D_a, and D_r. If any two of these three

TABLE XI. VALUES OF ΔH^* AND ΔS^*

Treatment	ΔH^* (cal.)	ΔS^* (e.u.)
Ether- and alcohol-extracted	8534	2.9
Alcoholic potash (15 sec.)	7800	0.9
Alcoholic potash (4 min.)	6520	−3.3
Alcoholic potash (15 min.)	6000	−5.3

coefficients have different heats of activation, a change in the distribution and average value of D_e penetration, s/b, will also change the apparent heat of activation, since the ratio of the amount of acid transported by radial and axial diffusion is dependent on D_e. The relation between the various diffusion coefficients, however, is too complex to justify a more detailed discussion. An important step to clarify this problem would be to separate axial and radial diffusion and study them under conditions where the influence of the epicuticle is eliminated.

One explanation of the change in ΔS^* with time of treatment would be that the differences in sorption rate along the fiber contribute to the entropy. When these differences are smaller, the entropy is decreased. No attempt is made here to develop this theory any further because of the limited experimental material.

Discussion

The sorption experiments with dyes and acids described in this paper show that the epicuticle has a great influence on the diffusion of ions across the phase boundary. The physicochemical nature of this barrier is difficult to explain on the basis of present knowledge, but there are some characteristic features which can be discussed. From the acid sorption experiments it can be concluded that the diffusion across the boundary layer (represented by D_e) can take place in two ways: either $D_e = 0$ where the epicuticle is intact, or $D_e \neq 0$ but $D_e \leq D_r$. In all parts where there is no epicuticle, $D_e = D_r$. Any change in the rate of sorption caused by a physicochemical change of the surface can then be explained in two ways. In certain areas where the epicuticle was originally intact, it is removed or changed so that $D_e = D_r$, while in other parts $D_e = 0$. The other explanation is that D_e for the intact epicuticle continually increases upon treatment from a low value and ultimately approaches the value of D_r. Thus, it can be either a continuous change of the diffusion through the epicuticle or a discontinuous change.

From the evidence given here the most plausible explanation is a continuous change of the diffusion rate. The increase in the heat of activation is more likely to be associated with a change in the nature of diffusion through the epicuticle than with a difference in the nature of axial and radial diffusion. The distribution of dyes over the fiber is more even after the treatments, which indicates an increased diffusion through the epicuticle. The diffusion of dye depends on the basicity of the dye, and the difference between treated and untreated wool increases with the basicity. This means that the diffusion through the epicuticle relative to the diffusion through the bulk of the fiber is dependent on basicity and that $D_e > 0$.

The dependence of the diffusion on basicity further suggests that the barrier is electrical in nature, which means that nonpolar or weakly polar substances might diffuse rather easily through the epicuticle if they have affinity for the fiber, whereas highly polar substances like trisulfonated dyes would diffuse hardly at all through the epicuticle. This leads to the same conclusion as drawn from frictional measurements [13] that the epicuticle originally is a weakly polar substance but becomes more and more polar under the action of alkali.

O'Reilly *et al.* [18] recently gave a theory that the position of the scales influences the rate of dye sorption, the distention of the scales being changed by processing the fibers. The most important result was that the rate of sorption was decreased when the fibers were steamed. Lagermalm *et al.* [10], however, showed that steaming influences the diffusion through the bulk of the fiber if the fibers were treated previously in an aqueous alkaline solution. The distention of the scales had, according to them, only very little influence on the diffusion. It is thus important to separate the increase of diffusion rate due to a change of bulk structure from that due to a change of surface structure.

Due to the heterogeneity of the epicuticle, the distribution of the dye over the fiber is very uneven in the beginning of the process. On continuing the dyeing a levelling process takes part, but it is impor-

tant to note that this takes a much longer time than the original exhaustion of the dye bath. The heterogeneity of the epicuticle thus mainly determines the dyeing time. This dyeing time is rather long, which means that practically all wool dyeing processes have to be discontinuous. Continuous dyeing processes require a rapid exhaustion and homogeneous fibers because there is no time for levelling, and have hitherto been restricted to rapidly levelling dyes and to vat dyes[3]. When the permeability of the epicuticle, however, is increased by treatment with alcoholic potash, it is possible to perform a level dyeing in 1–2 min. with most dyes. The problem of continuous dyeing therefore hinges on the possibility of making the permeability of the surface homogeneous, either by treating the fibers or by selecting proper dyes and dye assistants. The change of the diffusion in the bulk, provided it is not localized to certain parts, is of much less importance and has much the same effect as a change in dyeing temperature.

Acknowledgment

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Relationship Between Various Surface Properties of Wool Fibers

Part IV: Wettability

Abstract

The wettability or the surface tension of wool fibers is dependent on the epicuticle. There are close relationships between friction, rate of diffusion of dyes and acids, and surface tension. The surface properties of the fiber can be changed without removing the epicuticle. Such change is thought to be due to an alteration of the molecular structure of the epicuticle.

WETTABILITY is a typical surface property. It is well known that wool fibers have poor wetting properties and that the wettability is increased considerably by chemical and mechanical treatments. Many antifelting processes, such as chlorination and also alcoholic potash treatments, are known to increase the wettability [13]. Treatments with aqueous alkali, boiling water [10], and ultraviolet radiation [9] have the same effect. Baxter and Cassie showed that virgin wool has a lower wettability than wool which has been subjected to normal processing. La Fleur [10] pointed out the sensitivity of wetting tests to modifications of wool fibers. These tests are, of course, for evaluation of surface modifications only.

The most common test for wettability is to measure the sinking time of a loaded yarn or fabric sample in a water solution having a specified surface tension (Draves' test [5]). This method is not satisfactory for measuring the surface tension of the fiber because the sinking time is not proportional to the surface tension of the fiber. Only one value of the surface tension of the fiber would be in equilibrium with the surface tension of the liquid; other values would cause the fibers to sink or float. Actually, the sinking test is a measure of the rate by which the air is driven out of the sample [17]. By changing the surface tension of the liquid until equilibrium is established—the solid will just about sink—the surface tension of the liquid becomes a measure of the surface tension of the solid [1]. This method would be difficult to use with pieces of fibers because the surface tension probably varies along the fiber. Preston [16] investigated the flotation of wool fibers, and found that there are differences in wettability between tip and root.

Another method was suggested by Schuyten *et al.* [19] which was claimed to give a measure of the surface tension of the fibers. This method was found to give good results, and is used here to measure the surface tension of the samples pretreated according to Part I [11].

The apparatus consisted essentially of an inclined plane (45°) to which a fabric could be clamped by two clamps some distance apart. The distance between the clamps formed a gap in an electrical circuit. The circuit included a magic eye. A few drops of a salt solution with a known surface tension were rolled down the fabric from clamp to clamp. If the solution had a lower surface tension than the corresponding surface tension of the fibers, the fibers were wetted and a trace of the solution was left on the fabric. The salt solution had a good conductance and the circuit was closed, which could be seen from the magic eye. If the solution had a higher surface tension than the corresponding surface tension of the fibers, there was no trace of the solution on the fabric and the circuit was still open. If a range of solutions having different surface tensions were prepared, the point of wetting could easily be found by a few trials.

In the present case the samples were in the form of loose fibers, and therefore another technique had to be used to produce the fiber surface. The fibers were cut finely in a Wiley mill and a thick layer was spread out on a Perspex plate, which was covered with a layer of a water-insoluble glue. After brushing away the loose fibers, a suitable surface was obtained. Water solutions of butyl alcohol of different concentrations were used as test solutions, as recommended by Schuyten *et al.* Surface tensions were measured by the ring method [7].

The surface tensions of the test solutions, which just wetted the different samples, are given in Table I. Measurements on three different plates from each sample gave similar results.

TABLE I. VALUES OF SURFACE TENSION OF TEST SOLUTIONS

Treatment	Surface tension (dynes/cm.)
Untreated	46
Ether-extracted	46
Ether- and alcohol-extracted	44
Alcoholic potash (15 sec.)	63
Alcoholic potash (4 min.)	71
Alcoholic potash (15 min.)	71

TABLE II. RESIDUAL OIL CONTENT (% OF DRY FIBER WEIGHT)

Treatment	Time of scouring: 6 min.	11 min.	16 min.	21 min.	Mean values
Ether- and alcohol-extracted	13.1	5.4	3.6	3.5	6.4
Alcoholic potash (15 sec.)	8.7	3.8	2.9	4.9	5.1
Alcoholic potash (4 min.)	10.6	5.8	1.9	2.4	5.1
Alcoholic potash (15 min.)	9.3	5.0	1.9	1.6	4.5

From the table is seen that the surface tension was higher for fibers treated with alcoholic potash. It should also be noted that extraction with alcohol decreased the surface tension, probably by removing some substance. This was pointed out by Jacobi [8], who found that clean fibers have the lowest wettability.

The increase of surface tension brought about by alcoholic potash treatments can be explained by a change of polarity of the surface layer. A weakly polar surface is not wetted by water, whereas a highly polar surface is wetted easily. The present results thus fit in with the theory given in Parts I–III ([11, 12] and p. 573, this issue) that alcoholic potash treatments change the polarity of the wool fiber surface.

It is well known that mineral oil, which is a typical nonpolar liquid, will stick tenaciously to virgin wool fibers and is almost impossible to remove by scouring. The fiber is "wetted" by the oil. If the wool fibers are chlorinated, it is much easier to remove the oil [6]. If the scourability of oiled samples is a measure of the "wetting" properties of mineral oil, the residual oil content after scouring would be expected to rank in opposite order to the values of surface tension given in Table I.

The scourability of the samples was measured by a modification of a method described by Dickinson and Palmer [4]. Small pieces of top weighing about 1 g. were put into glass tubes. The tube was completely filled with the sample and paraffin oil was added. A wash solution (2 ml. of Berol WMA-B09 in 10 liters of water) was then pumped through the tube at a rate of 0.4 liter/min. The wash solution was not circulated, so that fresh solution was continually pumped through the tube. The experiments were made at room temperature. After a certain time the top was removed from the tube, dried, and extracted with ether. Three replicates of each combination of treatment and scouring time were made. The means of the residual oil contents are given in Table II.

Residual oil content is plotted against surface tension in Figure 1. The experimental error was rather large, but a statistical analysis of the logarithms of the data showed that the downward slope of the mean values with increasing time of treatment is significant. The residual oil content thus ranks in opposite order to the values of surface tension given in Table I. These results are a further verification of the theory that the surface layer changes from a less polar to more polar character when the fibers are treated with alcoholic potash or are chlorinated. The rather paradoxical behavior of untreated and chlorinated wool fibers towards mineral oil is also easily explained by this theory.

Discussion

This work was intended to show the close relationship between the various properties of wool fibers which are affected by a surface reaction, such as treatments with alcoholic potash. There are three main surface properties which determine the technological behavior of the fibers to a large extent and which have been the subject of investigation in this series of papers—namely, surface friction, surface tension, and diffusion across the surface layer. The relationships between the experimental data obtained for these properties after various treatments are shown in Figures 2–4. It is seen from the graphs that there are marked relations between these properties. There is, of course, no reason to expect strict linear relationships. The relations, however, are marked enough to justify the conclusion that changes in these properties have the same source—namely, an alteration of the physicochemical properties of the epicuticle.

The relation between surface tension and surface friction is interesting because it gives corroborative evidence for the theories put forward by Bowden and collaborators [3] of the physicochemical nature of the friction. They attributed the friction to an attraction between molecules, and they showed that this attraction might be related to surface tension.

"Since the surface tension is a measure of the attractive force between the metal atoms and the fric-

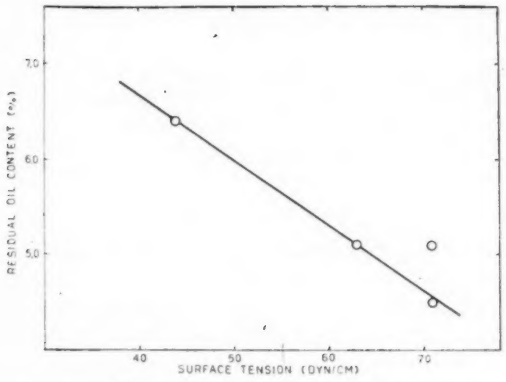

FIG. 1. *Relation between residual oil content after scouring and surface tension of the fibers.*

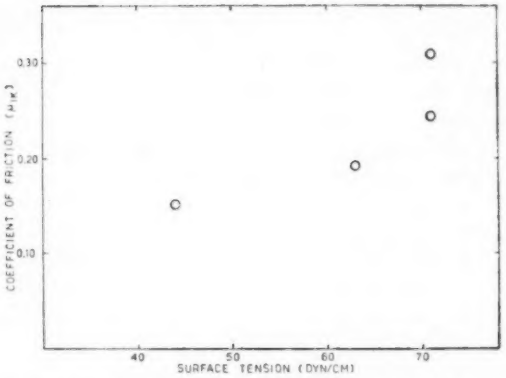

FIG. 2. *Relation between coefficient of friction and surface tension of fibers after various treatments.*

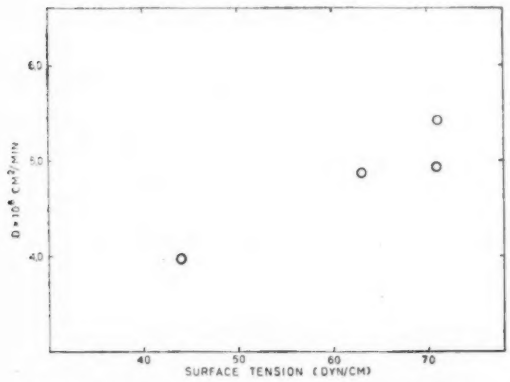

FIG. 3. *Relation between diffusion coefficient and surface tension of fibers after various treatments.*

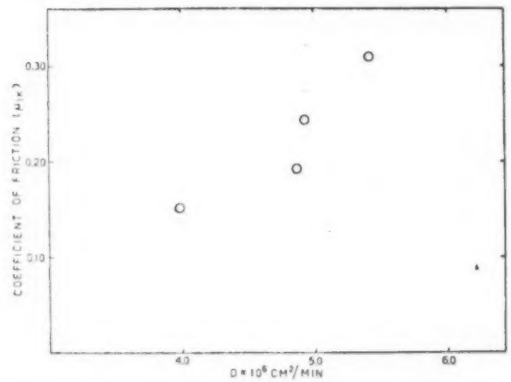

FIG. 4. *Relation between coefficient of friction and diffusion coefficient after various treatments.*

tion is due to the attraction between the metal atoms on the two adjacent surfaces, we might expect to find a correlation between them and it is interesting to see that this is so" ([3], p. 157).

The physicochemical nature of the alteration of the epicuticle is difficult to interpret on the basis of the present data because we still lack knowledge of the chemical structure of the epicuticle. All the evidence, however, points to a change in the polarity of the surface, regardless of which chemical reaction causes this change.

When the surface is brought into contact with the alkaline reagent, it is only a matter of seconds for the alteration of the epicuticle to take place. This behavior is suprising because one of the most striking properties of the epicuticle, which was the reason for its discovery, is its resistance to dissolving in alkaline reagent. Two plausible explanations for this rather paradoxical behavior may be given: (*1*) there might be a thin surface layer only a few molecules thick which covers the epicuticle and which is sensitive to alkali; (*2*) some functional groups of the epicuticle might be changed by means of the alkaline reagent without affecting the main molecular structure, which still might be very resistant to this reagent.

The immediate implication of this reasoning is that the epicuticle isolated by conventional means is not equivalent to the original surface which determines the behavior of the fiber. This means that it is difficult to draw any conclusions as to how the fiber will behave in processing from the properties of the isolated epicuticle. The surface properties of the fibers could thus be changed without removing the epicuticle.

The importance of the surface properties of wool fibers in the processing of the fibers need not be stressed. Friction plays an important role in the

mechanical processing and in the felting properties of the fibers. Surface permeability controls the sorption and desorption of dyes, acids, and other electrolytes. Surface tension determines the wettability and scourability of fibers. The properties and the serviceability of the finished fabric might also be influenced by the surface properties.

The raw material which comes to a mill will show a great variation in surface properties both within fibers, between fibers, and between greater or smaller assemblies of fibers. These variations will further be increased during processing by uneven treatments in localized parts. Examples of progressive surface damage have been given by O'Reilly *et al.* [15] and Royer *et al.* [18], who measured the rate of exhaustion of dyes, and by Baxter and Cassie [2], who measured the wettability. Uneven treatments are difficult to avoid because of the sensitivity of the epicuticle, and are apt to cause much trouble in making a homogeneous product. By introducing a treatment in the early stages of processing which would make surface properties more uniform and obliterate the effect of all previous and subsequent treatments, much of the trouble might be avoided, and entirely new methods, such as continuous dyeing, might be possible.

An important question to answer, if such a procedure is introduced, would be how the properties of the finished fabric would be affected. Too little is known about this yet, although such treatment has been used for a long time to make fabrics nonfelting. When a knitted garment is treated in alcoholic potash, the handle becomes very harsh. After it has been washed a few times, this harshness largely disappears. Mercer [14] showed that if fibers treated with alcoholic potash are given a subsequent treatment with Velan PF, the increased friction is reduced to its original low value. It is generally assumed that the effect of this treatment is obtained by attaching a hydrocarbon chain to the fiber. A fiber treated with Velan PF will furthermore have a low wettability, and it seems likely that the surface will become less polar because of the treatment.

This opens up an interesting possibility. If the alkaline treatment changes functional groups in the structure of the epicuticle, this reaction might be made reversible, and it might be possible to restore the original properties of the surface by an appropriate reaction—*e.g.*, by Velan PF. If such controlled changes in the surface properties can be made at will during processing, this would be a key to important improvements in wool fiber technology. A successful application of such treatments, however, hinges on a more profound knowledge of the chemical structure of the epicuticle. The solution of this problem is, therefore, one of the most important tasks for future wool fiber research.

Acknowledgments

My thanks are due to Professor N. Gralén for his unfailing interest and helpful advice, to Mrs. E. Bernehed, who skillfully carried out the experimental work, and to the board of the Institute for permission to publish this paper. The International Wool Secretariat, London, sponsored part of this work.

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The Laws of Static Friction

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Abstract

The relation $F = aR^n$ between the frictional force and normal reaction is found to hold for fibers, and it is proposed to replace Amontons' law by this form. The friction index, n, is found to lie between 0.80 and unity. The significance of this relation is discussed in terms of the cohesion theory of friction. A satisfactory interpretation can be given if it is assumed that the areas of contact are determined by the visco-elastic properties of the surfaces. A comparison of this relation with that of Gralén's is made. Two important consequences arise from the adoption of this friction law: the frictional force is no longer independent of the apparent area of contact; and, in the case of friction of a string or fiber wrapped around a cylinder, the so-called "coefficient of friction" depends upon the initial tension and also upon the cylinder radius.

Introduction

The limiting frictional properties of two surfaces in contact are usually described by two laws: (*1*) the frictional force, F, just sufficient to separate the surfaces which are subjected to a normal force, R, is given by $F = \mu R$, where μ, the coefficient of friction, is a constant (Amontons' law); and (*2*) F is independent of the apparent area of contact. Much fundamental research has been made in recent years on the mechanism of the friction process, chiefly by Bowden and his coworkers. As a result of this, we have a greater understanding of the operation of these laws, particularly in the case of metallic surfaces, where they have been confirmed over large ranges of R values. Occasional exceptions can be attributed to the occurrence of surface contaminations, chiefly oxide films.

Because of their technical importance, the frictional properties of textile fibers have also been studied a great deal, and here the story is quite different. The coefficient μ is no longer a constant, but is found to increase as the load R decreases. Since Amontons' law, $F = \mu R$, is no longer valid, various attempts have been made to replace it by a more general expression. The present paper is concerned with certain of these empirical relationships and their interpretation in terms of the current theory of friction. Consequences arising from the acceptance of one form of the F-R relation are also discussed.

Experimental Studies of the Variation of the Coefficient of Friction

A number of different methods of studying fiber friction are described in the literature, most of which report the variable character of the coefficient μ as defined by the ratio F/R. Only those which are concerned in the subsequent discussion will be mentioned here.

Martin and Mittelmann [4] made a thorough investigation of the friction of wool fiber-keratin surfaces by measuring the initial and final tensions, T_o and T, in a fiber when it was on the point of slipping around a keratin cylinder. Using the standard relation $T = T_o e^{\mu\theta}$, where θ is the angle of wrap, they measured μ for a large range of T_o values and expressed the variation which they found in the empirical form $\mu = A - B \log T_o$ (A and B being constants). They could not interpret this dependence, but emphasized that it represented a failure of Amontons' law.

Gralén [1] and his coworkers used a twist-slip method in which one fiber is twisted around the other with a small helical angle and the force required to slide them over each other is measured for various loads, R. He expressed the results in the form $F = CR + DR^\alpha$, and for Terylene he found the experimental results to be fitted best by a value of $\alpha = 0.3$ (although it would appear that there is quite a latitude in the values of α which would also give a reasonable fit). He later modified this result for Terylene and also nylon to give $\alpha = 0.5$ (private communication).

Lincoln [3] measured the friction of a nylon hemisphere against a nylon plane surface and its variation with R, and concluded that $F \propto R^{2/3}$.

Howell and Mazur [2] studied the dependence on R when two fibers are at right angles to each other and expressed their results in the form $F = aR^n$.

They obtained these typical values of n: 0.80 for drawn nylon, 0.90 for undrawn nylon, 0.95 for cellulose acetate, and 0.91 for viscose rayon.

In order to interpret these results and understand how Amontons' law has broken down, it is necessary to refer to Bowden's cohesion theory of friction.

Plastic and Elastic Deformations in the Friction Theory

According to the cohesion theory, when two surfaces are pressed together with a force R, contact is made only at the tips of a number of irregular asperities, even in the case of highly polished surfaces. Because of the small real area of contact, the pressure developed even for a small value of R is sufficiently high for the yield point of the material to be exceeded. This results in a plastic flow of the contact region, thus extending the area, and this continues to grow until the pressure has fallen to the yield value p_y, at which point the plastic flow ceases and the load R can be supported elastically. The area of real contact, A, is thus related to the load by the relation $A = R/p_y$. Owing to the occurrence of plastic yield and flow, the material from the asperities of one surface is in such intimate contact with that from the opposing surface that opportunity for welding occurs. In order to move one surface relative to the other, a tangential force, F, is required to completely shear these welded junctions, and this force is identified with the friction force. It is related to the area of contact by the relation $F = SA$, where S is the shear strength of the junctions. Then, $F = S\ (R/p_y)$, so that F is proportional to R (Amontons' law), and the coefficient of friction is $\mu = S/p_y$. If the cohesive forces at the junctions are the same as in the interior of the bulk material, then the weld is a true one and S is the same as the shear strength of the bulk material.

The relation $F = \mu R$, which can be regarded as the special case of $F = aR^n$ when $n = 1$, is now linked with the notion of plastic deformation of the contact area. In the case of metals with a relatively high elastic modulus, the elastic deformation on the application of the load is small and is insufficient to produce an area large enough to bring the pressure down below the yield value. As a result, plastic flow ensues. Now, in the case of softer materials such as the high polymers of textile fibers, with a much lower elastic modulus, the elastic deformation for a given load is very much larger and can be sufficient to support it without further extension. This deformation can be calculated with perfectly elastic bodies —*e.g.*, with a sphere on a plane the contact area is proportional to $R^2/3$, with two cylinders at right angles it is also proportional to $R^2/3$, whereas with two parallel cylinders this becomes $R^{\frac{1}{2}}$. If it is assumed that cohesive forces operate across the contact area, then if S is the shear strength of the cohesions we can write as before $F = SA = kSR^n$, where k is a constant depending upon the dimensions and elastic properties of the materials and the index n is less than unity. In this way the empirical relation $F = aR^n$ can be interpreted, and, since it includes Amontons' law $F = \mu R$ as the special case of $n = 1$, it is a more general formulation of the first law. The breakdown of the law $F = \mu R$ is now recognized as being a consequence of the area of contact being determined largely or partly by elastic properties. In practice, the area of contact is determined by the transverse rheological properties and these may be quite complex. Thus, from the writer's own measurements the result to be expected from ideally elastic bodies is $F = aR^{\frac{2}{3}}$, but values from 0.8 to 0.96 have been obtained, indicating that we have neither pure plastic flow nor ideally elastic deformation but something in between, the index n approximately indicating the relative importance of the two modes of deformation. Instead of using the single term in $F = aR^n$, Gralén attempted to divide the frictional force into that due to the plastic area of contact and that due to the elastic deformation; thus, $F = CR + DR^{\frac{2}{3}}$. The two expressions refer fundamentally to the same mechanism—the area deformation under load R—but whereas the former gives, in effect, the equation of the deformation-R curve, the latter analyzes it into two curves, one plastic and the other ideally elastic.

Incidentally, it should be noted that in cases where the deformation is nearly elastic the index n depends upon the method of measurement and in the case of cylinders can be 0.66 (Howell's method) or 0.5 (Gralén's method).*

Applications of the Friction Law, $F = aR^n$

In this section will be considered certain consequences which arise when Amontons' law is replaced by $F = aR^n$.

* In other cases, as n approaches unity the difference will be less noticeable.

Dependence upon Apparent Area of Contact

Let two plane surfaces of areas A_1 and A_2 of the same material in the same physical condition slide upon a common surface and let them carry the same load R. Let us assume that the asperities are uniformly distributed and of the same size and shape: N_1 in the area A_1, and N_2 in A_2. Then, $N_1/N_2 = A_1/A_2$. If the friction law for each asperity is $f = ar^n$, where r is the reaction on each, then the measured frictional force $F = Nf$ if the contacts all yield at the same time. Since $r = R/N_1$ in the first case and R/N_2 in the other, we have

$$\frac{F_1}{F_2} = \frac{N_1 a\left(\frac{R}{N_1}\right)^n}{N_2 a\left(\frac{R}{N_2}\right)^n} = \left(\frac{N_1}{N_2}\right)^{1-n} = \left(\frac{A_1}{A_2}\right)^{1-n},$$

so that for the same load R the frictional forces are not the same in the two cases but increase as the apparent area increases at a rate depending upon n. In the case of Amontons' law, $n = 1$ and the force is independent of the apparent area—*i.e.*, law 2 is a natural consequence of the acceptance of $F = \mu R$ but only holds in that particular case.

Friction Around a Cylinder

The relation $\frac{T}{T_o} = e^{\mu\theta}$ used by Martin and Mittelmann in their study on wool is based on the assumption $F = \mu R$. If $F = aR^n$ is used in the analysis, this expression is replaced by

$$\left(\frac{T}{T_o}\right)^{1-n} = 1 + (1-n)a\left(\frac{\rho}{T_o}\right)^{1-n}, \qquad (1)$$

or, in the limit as n tends to unity,

$$T = T_o e^{a\theta(\rho/T_o)^{1-n}}. \qquad (2)$$

Here ρ is the radius of the cylinder. Hence, the ratio T/T_o is not constant but depends upon T_o and also upon ρ; only in the case of $n = 1$ is it independent of these quantities.

By examining the proposed exponential expression with the standard one, it will be seen that

$$\mu = a\left(\frac{\rho}{T_o}\right)^{1-n}$$

or

$$\log \mu = A' - B' \log T_o. \qquad (3)$$

Martin and Mittelmann's results on wool have been used to examine these relations. Good agreement is obtained when they are fitted to equation (1) using a value of $n = 0.75$,* and the plot of equation (3) shows a better agreement than Martin and Mittelmann's empirical $\mu = A - B \log T_o$.

There will be no need to emphasize the importance in the processing of yarn of the dependence of T upon the cylinder radius.

Coefficient of Friction

In $F = \mu R$ the constant μ is dimensionless, but the constant a in the more general expression $F = aR^n$ must have dimensions of $[\text{force}]^{1-n}$. Also, in the cylinder problem F and R refer to forces per unit length, and this results in the constant having dimensions of $[\text{force/length}]^{1-n}$.

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* The author is indebted to Dr. A. C. Benson for this figure.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Flexural Recovery of Textile Fabrics

IMPERIAL CHEMICAL INDUSTRIES LTD.
Dyestuffs Division
Manchester, England
March 6, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The fabric liveliness test developed by Dr. J. W. Ballou and described by R. M. Hoffman and L. F. Beste (TEXTILE RESEARCH JOURNAL **21**, 66–77 (1951)) aroused considerable interest here, as work of a similar nature is proceeding in these laboratories. Criticism must, however, be made of the treatment given.

It was stated that for the opening of the fabric the angle θ traversed in time t is given by

$$\theta = \frac{1}{2}\frac{T}{I}t^2, \tag{1}$$

where T is the accelerating torque and I the moment of inertia of the sample.

This fundamental relation is only applicable when the accelerating torque T is constant, and is analogous in linear motion to the equation for free fall under gravity—*i.e.*, under constant accelerating force. The authors postulated, however, that the torque is a function of θ, decreasing as the sample swings open, and proceeded to make the substitution

$$T \sim G/\theta \tag{2}$$

(where G is the fabric stiffness) in equation (1).

In the first place, the relations (1) and (2) are incompatible. Also, equation (2) is itself unsound since it implies an infinite torque when θ is zero—*i.e.*, in the initial deformed position. Assuming that the torque is linearly related to the angle of bend, the relation should be

$$T \sim G(180^\circ - \theta), \tag{3}$$

or

$$T = k\alpha, \tag{4}$$

where k is a constant and α is the angular deflection from the unbent position.

The equation of motion can then be written in the form

$$I\frac{d^2\alpha}{dt^2} + \eta\frac{d\alpha}{dt} + k\alpha = 0, \tag{5}$$

where η is a damping term, which includes both fiber and air damping components.

The solution of equation (5) depends on the values of the constants I, η, and k. In the case where $\eta^2 < 4Ik$, it represents a damped oscillation, the frequency of which is given by

$$f = \frac{1}{2\pi}\sqrt{\frac{4Ik - \eta^2}{4I^2}}. \tag{6}$$

The solution is given in any textbook dealing with damped vibrations.

If $4Ik$ is large compared with η^2, the damping is low and we have

$$f \sim \sqrt{\frac{k}{I}} \sim \sqrt{\frac{G}{I}}$$

—*i.e.*, the frequency of oscillation will be proportional to $\sqrt{G}$. A correlation between liveliness and stiffness is thus to be expected.

In the recorder trace included in their paper, Hoffman and Beste showed only a single swing, and there was no indication as to whether there was a damped

oscillation or whether the damping was greater than the critical value. Presumably the trace had been idealized, in so far as it showed 100% recovery and a linear relation between light intensity and time. Preliminary tests in these laboratories, using an initial bend of 90°, have in all cases shown a damped oscillation together with a creep component.

M. M. Cross

Thermodynamics of Stretching Cellulosic Fibers

Textile Research Institute
Princeton, New Jersey
April 3, 1953

To the Editor
Textile Research Journal

Dear Sir:

It was first shown by Meyer and Lotmar [8] that the elastic modulus of truly elastic deformation for cellulose fibers is considerably lower than that calculated from the stretching of the cellulose molecule. The main reason for this difference is that the direction of applied stress in stretching the fiber is not the direction of the long axis for many molecules in the substance. When the substance is stretched, the molecules tend to align themselves in the direction of stress, forming a different arrangement by uncoiling or bending. Such rearrangement involves a change in entropy of the system. Entropy changes of this type have been investigated for rubber [4], keratin fibers [2, 6, 10], and nylon [10]. The sign (positive or negative) of the entropy effect for cellulosic fibers has been indicated by Meyer and Lotmar [8] and by Anderson [1], but no systematic investigation of the thermodynamic aspects of the stretching of cellulose fibers has been reported.

The thermodynamic equations relating to reversible changes of state in stretching fibers have been summarized by Katz [5]. For a small reversible change in length at constant temperature and pressure, the force which the fiber exerts is given by the equation

$$F = (\partial U/\partial L)_{TP} - T(\partial S/\partial L)_{TP} + P(\partial V/\partial L)_{TP} + \mu(\partial n/\partial L)_{TP}, \quad (1)$$

in which $(\partial U/\partial L)_{TP}$ is the change in potential energy of the fiber, $(\partial S/\partial L)_{TP}$ is the change in entropy, $(\partial V/\partial L)_{TP}$ is the change in volume, and $(\partial n/\partial L)_{TP}$ is the change in mole fraction of fiber in water with changes in length of the fiber. The last term in this equation, in which μ is the partial molal free energy of the fiber in water, takes into account the energy changes accompanying the change of water in the fiber system with stretching. In the absence of experimental evidence to the contrary, this term is presumed to be negligible. Meyer and Van der Wyk [9] have shown that at low pressures $P(\partial V/\partial L)_{TP}$ is very small compared to $(\partial U/\partial L)_{TP}$.

Thus, if the last two terms in equation (1) are small, the force exerted by the fiber is simply the result of a change in potential energy of the fiber and of a change in entropy. If the entropy term is zero, all the stress exerted by the elastic body is due to energy stored up by various mechanisms in the fiber molecules [7]. If the entropy changes with stretching, the transition to a more ordered or to a less ordered state or arrangement in the fiber is indicated, depending upon whether the entropy decreases or increases, respectively.

Separation of the energy and entropy contributions can be accomplished by measuring the change in force produced by changing the temperature of the stretched fiber, for it can be shown by classical thermodynamics that

$$(\partial S/\partial L)_{TP} = -(\partial F/\partial T)_{LP}.$$

Since the total force, F, is observed in the experiment which also measures $(\partial F/\partial T)_{LP}$, both $(\partial U/\partial L)_{TP}$ and $T(\partial S/\partial L)_{TP}$ in equation (1) can be evaluated if the assumptions mentioned above are valid.

While at the Institute of Textile Technology in Charlotesville, Va., the present authors made measurements of this type on cotton and viscose fibers

TABLE I. ENTROPY AND ENERGY CONTRIBUTIONS TO TOTAL FORCE FOR WET COTTON AND VISCOSE FIBERS

Elongation (%)	$(\partial F/\partial T)_{LP}$ (dynes/°C)	F (dynes)	$(\partial U/\partial L)_{TP}$ (dynes)	$T(\partial S/\partial L)_{TP}$ (dynes)
Cotton fibers				
2.6	−1.25	68	474	406
4.7	−2.14	307	953	646
Viscose rayon				
1.7	−0.92	332	600	268
3.9	−1.05	446	754	308
4.8	−1.07	705	1017	312

in the wet state [3]. The apparatus used consisted essentially of a small glass thermostat in which the temperature could be rapidly varied by running in hot or cold water. Force on the fiber was measured by means of a mechano-electronic transducer tube (RCA Type 5743). The fiber mounting was of Pyrex glass arranged to minimize thermal expansion errors. Stretching of the fiber was accomplished with a micrometer caliper. Temperature was measured with a thermocouple and a Leeds & Northrup Type K potentiometer, which was also used to read the output of the transducer tube.

Changes in force due to stress relaxation during the measurements tended to cause inaccuracies in the results, especially at high extensions. These could be reduced by allowing the fiber to relax for an hour or two before changing its temperature and by carrying out the temperature cycle rapidly. In this way, the results shown in Table I were obtained.

These results are noteworthy in two respects. In the first place, for both cotton and rayon the temperature coefficient of force at constant length is negative, indicating an increase in entropy with stretching. Apparently some existing structure in the fiber must be broken up before the well-known orientation effects due to stretching can take place. The mechanism of this structural change is not revealed by measurements of the type reported herein. It may be that at higher strains the entropy decreases again as orientation effects take place. Unfortunately, measurements at high strains are rendered difficult and inaccurate by the stress relaxation process.

The second point of interest is the observation that in cotton most of the potential energy stored up during stretching is necessary to overcome the entropy or structural changes that take place during contraction. This is indicated by the near equality in the values of the potential energy and entropy terms. In viscose rayon more of the internal potential energy is available to overcome external forces which might prevent elastic recovery.

It is hoped that these observations will stimulate additional interest in this field of textile research.

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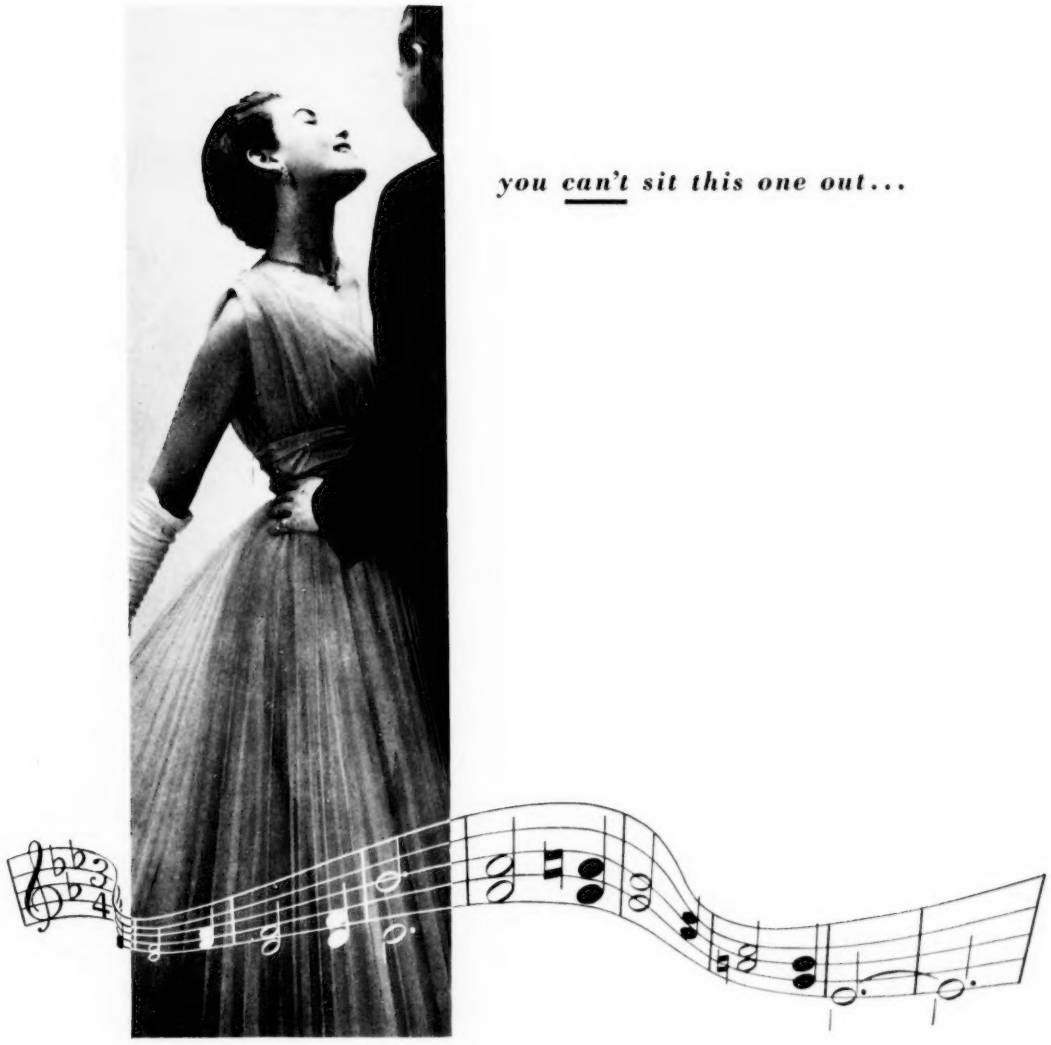
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